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Short Introduction to Relations Between Thermodynamic Quantities

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Short Introduction to Relations Between Thermodynamic Quantities

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Abstract

Thermodynamic quantities, such as pressure and internal energy, and their derivatives, are used in many applications. Depending on application, a natural set of quantities related to one of four thermodynamic potentials are typically used. For example, hydro-codes use internal energy derived quantities and Equation of State work often uses Helmholtz free energy quantities. When performing work spanning over several fields, transformations between one set of quantities and another set of quantities are often needed. A short, but comprehensive, review of such transformations are given in this report.

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Nomenclature

EOS Equation of State. Relations providing, for example, pressure and internal energy as a function of density and temperature.

SESAME A format for tabular EOS information.[1] At a minimum the internal energy and the pressure are tabulated on a rectangular grid of density and temperature.

ALEGRA The Arbitrary-Lagrangian-Eulerian General Research Applications (ALEGRA) code is a large-deformation shock physics code created by researchers at Sandia National Laboratory.

CTH A multi-material, Eulerian, large-deformation, strong shock wave, solid mechanics code developed at Sandia National Laboratories.

Internal energy, E A thermodynamic potential appropriate for isolated systems. The natural variables are entropy, S, and volume, V. If the entropy and volume are held constant, the system will evolve to an equilibrium state (pressure, P, and temperature, T) with minimum internal energy.

Helmholtz free energy, F A thermodynamic potential appropriate for closed systems in a reservoir (can keep temperature constant) but without exchange of mechanical work. The natural variables are temperature, T, and volume, V. If the temperature and volume are held constant, the system will reach the equilibrium state (pressure, P, and entropy, S) with the minimum Helmholtz free energy.

Gibbs free energy, G A thermodynamic potential appropriate for phase transitions. The natural variables are temperature, T, and pressure, P. If the temperature and pressure are held constant, the system will reach its equilibrium state (volume, V, and entropy, S) at the minimum Gibbs free energy.

Enthalpy, H A thermodynamic potential appropriate for constant pressure processes. The natural variables are entropy, S, and pressure, P. If the entropy and pressure are held constant, the system will reach its equilibrium state (volume, V, and temperature, T) at the minimum enthalpy.

Extensive variable A variable dependent on the amount of material present, e.g., specific volume, V, and entropy, S.

Intensive variable A variable independent of the amount of material present, e.g., pressure, P, and temperature, T.

Hugoniot The collection of points in thermodynamic phase space describing the final states achievable by a shock from a specific initial state. The principal Hugoniot is the Hugoniot from the ambient state. Secondary Hugoniots can be obtained from pre-shocked states. Note that the Hugoniot is not a thermodynamic path. An experiment cannot follow the Hugoniot. Only the final state of a shock experiment is on the Hugoniot.

Rayleigh line The line in thermodynamic $P - V$ space that connects the initial and final state of a shock, that is, the two points on the Hugoniot connected by a shock. The states in the shock profile of an abrupt shock lay on the Rayleigh line. If the profile is smeared out, the profile states for a normal material lay on a curve below the Rayleigh line in $P - V$ space, with the initial and final state on the Rayleigh line and the Hugoniot.

Isotherm A thermodynamic path where the temperature is held constant.

Isobar A thermodynamic path where the pressure is held constant.

Isochore A thermodynamic path where the volume/density is held constant.

Isentrope A thermodynamic path where the entropy is held constant.

Chapter 1

Introduction and Motivation

Even a person well versed in the theory of Thermodynamics can become completely overwhelmed when starting to use these quantities in a practical, hands-on, setting, such as writing computer code to determine phase equilibrium. This tutorial is based on my own struggles to find the correct combinations of thermodynamic quantities to use in specific situations, in particular while programming new materials models into hydro-codes. I am focusing on tools and strategies to use for deriving useful relations between thermodynamic derivatives. Another, more general, but very practical, introduction to the topic is available from Rebecca Brannon, University of Utah.[2]

Chapter 2

Thermodynamic Potentials

The four thermodynamic potentials

The first and second laws of thermodynamics

The four thermodynamic potentials are derived from the first and second laws of thermodynamics:

$$dE = -PdV + TdS\,. \tag{2.1}$$

In this equation E is the internal energy, P the pressure, V the volume, T the absolute temperature, and S the entropy. The pressure and temperature are independent of the amount of material present, they are *intensive* variables. In contrast, the internal energy, volume, and entropy, are *extensive* variables and depend on the amount of material present. Extensive variables are often measured as per quantity of material, for example per kilogram or per mole. This is indicated by adding a “specific” in front of the quantity, for example, specific internal energy (J/kg) and specific volume (m^3/kg). It is often helpful to keep in mind if a variable is intensive or extensive. All four thermodynamic potentials are extensive variables, as can be verified from the definitions below.

Internal energy $E(V,S)$:

Equation 2.1 directly gives

$$\left.\frac{\partial E}{\partial V}\right|_S = -P \qquad \text{and} \qquad \left.\frac{\partial E}{\partial S}\right|_V = T\,. \tag{2.2}$$

The cross second derivative gives one of Maxwell's relations:

$$\frac{\partial^2 E}{\partial V \partial S} = -\left.\frac{\partial P}{\partial S}\right|_V = \left.\frac{\partial T}{\partial V}\right|_S \equiv -\frac{T}{V}\Gamma\,, \tag{2.3}$$

where the last equality defines the Grüneisen parameter, Γ. The other two second derivatives,

$$-\left.\frac{\partial P}{\partial V}\right|_S \equiv \frac{B_S}{V} \qquad \text{and} \qquad \left.\frac{\partial T}{\partial S}\right|_V \equiv \frac{T}{C_V}\,, \tag{2.4}$$

defines the isentropic bulk modulus, B_S, and the specific heat, C_V, respectively.

Helmholtz free energy $F(V,T)$:

Helmholtz free energy is defined as

$$F = E - TS\,. \tag{2.5}$$

Reformulating the fundamental thermodynamic relation, Equation 2.1, in terms of the Helmholtz free energy gives

$$dF = dE - TdS - SdT = -PdV - SdT\,. \tag{2.6}$$

Equation 2.6 directly gives that

$$\left.\frac{\partial F}{\partial V}\right|_T = -P \qquad \text{and} \qquad \left.\frac{\partial F}{\partial T}\right|_V = -S\,. \tag{2.7}$$

The cross second derivative gives one of Maxwell's relations:

$$\frac{\partial^2 F}{\partial V \partial T} = -\left.\frac{\partial P}{\partial T}\right|_V = -\left.\frac{\partial S}{\partial V}\right|_T \equiv -\alpha B_T\,, \tag{2.8}$$

where the last equality defines the thermal expansion coefficient,

$$\alpha \equiv \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_P\,, \tag{2.9}$$

with B_T defined next. The other two second derivatives,

$$-\left.\frac{\partial P}{\partial V}\right|_T \equiv \frac{B_T}{V} \qquad \text{and} \qquad -\left.\frac{\partial S}{\partial T}\right|_V \equiv -\frac{C_V}{T}\,, \tag{2.10}$$

defines the isothermal bulk modulus, B_T, and the specific heat at constant volume, C_V, respectively. Note the congruence with the definition via the internal energy above.

Gibbs free energy $G(T,P)$:

Gibbs free energy is defined as

$$G = F + PV = E - TS + PV\,. \tag{2.11}$$

Reformulating the fundamental thermodynamic relation, Equation 2.1, in terms of the Gibbs free energy gives

$$dG = dF + PdV + VdP = -SdT + VdP\,. \tag{2.12}$$

Equation 2.12 directly gives that

$$\left.\frac{\partial G}{\partial T}\right|_P = -S \qquad \text{and} \qquad \left.\frac{\partial G}{\partial P}\right|_T = V\,. \tag{2.13}$$

The cross second derivative gives one of Maxwell's relations:

$$\frac{\partial^2 G}{\partial T \partial P} = - \left.\frac{\partial S}{\partial P}\right|_T = \left.\frac{\partial V}{\partial T}\right|_P \equiv V\alpha \,, \tag{2.14}$$

where the last equality defines the thermal expansion coefficient, conforming to the definition via the Helmholtz free energy. The other two second derivatives,

$$-\left.\frac{\partial S}{\partial T}\right|_P \equiv -\frac{C_P}{T} \qquad \text{and} \qquad -\left.\frac{\partial V}{\partial P}\right|_T \equiv \frac{V}{B_T} \,, \tag{2.15}$$

defines the specific heat at constant pressure, C_P, and the isothermal bulk modulus, B_T, respectively. Note the congruence with the definition via the Helmholtz free energy above.

Enthalpy $H(S,P)$:

Enthalpy is defined as

$$H = E + PV \,. \tag{2.16}$$

Reformulating the fundamental thermodynamic relation, Equation 2.1 gives

$$dH = dE + PdV + VdP = TdS + VdP \,. \tag{2.17}$$

Equation 2.17 directly gives that

$$\left.\frac{\partial H}{\partial S}\right|_P = T \qquad \text{and} \qquad \left.\frac{\partial H}{\partial P}\right|_S = V \,. \tag{2.18}$$

The cross second derivative gives one of Maxwell's relations:

$$\frac{\partial^2 H}{\partial S \partial P} = \left.\frac{\partial T}{\partial P}\right|_S = \left.\frac{\partial V}{\partial S}\right|_P \equiv VT\frac{\alpha}{C_P} = T\frac{\Gamma}{B_S} \,, \tag{2.19}$$

where the last equalities conforms to the definitions via the other thermodynamic potentials. The other two second derivatives,

$$\left.\frac{\partial T}{\partial S}\right|_P \equiv \frac{T}{C_P} \qquad \text{and} \qquad \left.\frac{\partial V}{\partial P}\right|_S \equiv -\frac{V}{B_S} \,, \tag{2.20}$$

defines the specific heat at constant pressure, C_P, and the isentropic bulk modulus, B_S, respectively (note the congruence with the definitions via the Gibbs and internal energies above).

Third derivatives of the thermodynamic potentials

Most materials have a much stronger density dependence than temperature dependence. For many applications, in particular in shock physics, third derivatives of the thermodynamic potentials with respect to volume are used in Equations of State and other materials models. Specifically we often use

$$B_T' = \left.\frac{\partial B_T}{\partial P}\right|_T = -1 - V \frac{\left.\frac{\partial^3 F}{\partial V^3}\right|_T}{\left.\frac{\partial^2 F}{\partial V^2}\right|_T} \tag{2.21}$$

and

$$B_S' = \left.\frac{\partial B_S}{\partial P}\right|_S = -1 - V \frac{\left.\frac{\partial^3 E}{\partial V^3}\right|_S}{\left.\frac{\partial^2 E}{\partial V^2}\right|_S} = 2\mathcal{G} - 1\,, \tag{2.22}$$

where the last equality defines the fundamental derivative, $\mathcal{G}$, used in the analysis of shock waves.

Use of thermodynamic potentials

Hydro-codes: Internal energy

The hydrodynamic equations are derived from mass, momentum, and energy conservation for isolated systems with no heat or work transferred between the environment and the system that is modeled. This would naturally lead to using the internal energy as the thermodynamic potential. However, the time update in a hydro-code updates volume and internal energy, and the subsequent determination of the state thus needs $T(V,E)$ and $P(V,E)$. The natural thermodynamic potential would actually be $S(V,E)$, since

$$\left.\frac{\partial S}{\partial V}\right|_E = \frac{P}{T} \qquad \text{and} \qquad \left.\frac{\partial S}{\partial E}\right|_V = \frac{1}{T}\,. \tag{2.23}$$

However, this thermodynamic potential is not commonly used.

The speed of sound c, which is a variable heavily used in hydro-codes, is related to the isentropic bulk modulus:

$$c^2 = VB_S = -V^2 \left.\frac{\partial P}{\partial V}\right|_S = \left.\frac{\partial P}{\partial \rho}\right|_S\,, \tag{2.24}$$

where $\rho = 1/V$ is the density.

Shock Physics: Internal energy or Enthalpy

Weak shocks are known to be nearly isentropic (see page 63 in Z&R[4]). In fact, one of the third derivatives of a thermodynamic potential discussed above, $\mathcal{G}$, is related to the weak entropy change in a weak shock:

$$\Delta S = -\frac{1}{6}\mathcal{G}\frac{c^2}{T}\left(\frac{\Delta V}{V}\right)^3 . \tag{2.25}$$

The natural framework for shock physics is thus a thermodynamic potential with entropy as a natural variable. The close connection between shock physics and hydro-code simulations makes internal energy the obvious choice. Since the enthalpy framework also have entropy as a natural variable, this framework is sometimes used in shock physics work (see for example Z&R[4] pages 50 and 64).

Shock physics data is often given as a linear relation between the shock velocity, U_s, and the particle velocity, u_p:

$$U_s = c_0 + s\, u_p\,, \tag{2.26}$$

for some constants c_0 and s. Using the jump conditions (Rankin-Hugoniot equations, page 46 in Z&R[4])

$$\begin{aligned} \rho_0 U_s &= \rho(U_s - u_p) & (2.27)\\ P_H &= \rho_0\, U_s\, u_p\,, & (2.28) \end{aligned}$$

where P_H is the pressure on the Hugoniot and $\rho_0 = 1/V_0$ is the reference density (where $P_H = 0$), we can derive

$$P_H = c_0^2 \frac{(V_0 - V)}{(V_0 - s(V_0 - V))^2}\,. \tag{2.29}$$

As the Hugoniot coincides with an isentrope to second order in volume near the reference volume, the value at V_0 of the first volume derivative of P_H is

$$\left[\left.\frac{\partial P_H}{\partial V}\right|_S\right]_{V_0} = -\,c_0^2\frac{1}{V_0^2}\,, \tag{2.30}$$

and we identify the coefficient c_0 in the $U_s - u_p$ relation as the sound speed at the reference volume. The second derivative at the reference volume is

$$\left[\left.\frac{\partial^2 P_H}{\partial V^2}\right|_S\right]_{V_0} = c_0^2\frac{4\,s}{V_0^3}\,, \tag{2.31}$$

which leads to

$$4\,s = -\left[V_0\frac{\left.\frac{\partial^2 P_H}{\partial V^2}\right|_S}{\left.\frac{\partial P_H}{\partial V}\right|_S}\right]_{V_0} = -\left[V_0\frac{\left.\frac{\partial^3 E_H}{\partial V^3}\right|_S}{\left.\frac{\partial^2 E_H}{\partial V^2}\right|_S}\right]_{V_0} = [2\mathcal{G}]_{V_0} = [B_S' + 1]_{V_0}\ . \tag{2.32}$$

The coefficient s in the $U_s - u_p$ relation is thus related to the third volume derivative of the internal energy.

Equation of State: Helmholtz free energy

Theoretical Equation of State work can be tied directly to statistical physics via the partition function, Z, and the Helmholtz free energy, $F(V,T) = -k_B T \ln Z$, where k_B is the Boltzmann constant. Many of the analytical models used in Equation of State work are derived from statistical physics, and it is thus natural that Equation of State work is performed in the Helmholtz free energy framework. However, for use in a hydro-code the Helmholtz free energy framework is not optimal, since we lack a direct connection to the internal energy. We see from Equation 2.5 that knowledge of the entropy, $S(V,T)$, via the second relation in Equation 2.7, gives us the translation between the available Helmholtz free energy and the needed internal energy. For use in a hydro-code, an Equation of State usually gives out $P(V,T)$ and $E(V,T)$. If determined from the same Helmholtz free energy, these two quantities will be *thermodynamically consistent*.

Experiments: Helmholtz and Gibbs free energies

One of the most straightforward types of experiments is changing temperature at standard, or other constant, pressure and measure volume change or heat capacity. Equally straightforward is to change pressure while keeping the temperature constant. Such isobaric and isothermal experiments are performed in the Gibbs free energy framework. Another type of experiments is using pressure to change volume at room, or other constant, temperature (for example, in a diamond anvil cell) or changing the temperature of a material and measuring pressure change at constant volume (especially for gases). These two type of experiments, isothermal and isochoric (constant volume), naturally fall into a Helmholtz free energy framework since $P(V,T)$ is measured while keeping one of the variables constant. The Helmholtz free energy also connects the experimentally determined $P(V,T)$ to the internal energy, $E(V,T)$, the two quantities usually tabulated in an EOS for use in a hydro-code. If the formulas for the pressure and internal energy are both determined from an Helmholtz free energy via Equations 2.7 and 2.5, they are *thermodynamically consistent*, and parameters fitted to the experimentally determined $P(V,T)$ curves would automatically yield a correct internal energy, up to a constant.

Phase transitions: Gibbs free energy

Another type of straightforward experiment is to observe phase transitions, either by changing the pressure at constant temperature or changing the temperature at constant (for example, ambient) pressure. These experiments fall naturally into the framework of Gibbs free energy since phase boundaries are most naturally given in a $P-T$ phase space. This is, of course, due to the fact that a material in a mixed phase, with several different phases present at the same time, still has a well defined pressure and temperature, due to the intensive nature of these two variables.

Chapter 3

Thermodynamic derivative relations

From the definitions of the four thermodynamic potentials in the previous chapter, every possible relation between thermodynamic derivatives can be derived. Consider that we have four thermodynamic potentials, E, F, G, H and four variables, V, T, S, P, that each can be in three positions, X, Y, Z: $\frac{\partial X}{\partial Y}\big|_Z$, and disregarding slight over counting, we have $8^3 = 512$ first and second order derivatives of the thermodynamic potentials. Finding the needed relationships between these derivatives can be daunting. This can often feel like a blind trial and error and easily leads to circular argumentation. The key to success is to keep track of what you need and what you have access to. Intermediate steps in the following derivations are the ones that came naturally to me.

Hydro-codes and Equations of State: Internal energy vs Helmholtz free energy

Equation of State work usually is performed within the Helmholtz free energy framework, with V and T as natural variables. However, to determine the state in an hydro-code, where V and E are the variables that are updated in every time step, $T(V, E)$ and $P(V, E)$ are needed. In order to translate between what is needed in an hydro-code and what is available, the EOS usually gives values for $E(V, T)$ and $P(V, T)$, and an inversion procedure is used between the given internal energy and volume and the sought temperature. For an EOS that will be used in hydro-codes, it is thus natural to also provide values for the four derivatives

$$\left.\frac{\partial E}{\partial V}\right|_T, \left.\frac{\partial E}{\partial T}\right|_V, \left.\frac{\partial P}{\partial V}\right|_T, \left.\frac{\partial P}{\partial T}\right|_V . \tag{3.1}$$

Due to the Maxwell relations these four derivatives are not independent, in fact, only three of four are. We can derive the isothermal volume derivative of the internal energy using the Helmholtz framework, or directly from the first and second law in Equation 2.1:

$$\left.\frac{\partial E}{\partial V}\right|_T = \left.\frac{\partial F}{\partial V}\right|_T + T \left.\frac{\partial S}{\partial V}\right|_T = -P + T \left.\frac{\partial P}{\partial T}\right|_V , \tag{3.2}$$

and, indeed, we see that two of the four derivatives are directly related. This equation is often used to investigate the thermodynamic consistency of tables listing $E(V, T)$ and $P(V, T)$.

For the isochoric (constant volume) thermal derivative of the internal energy we again use Helmholtz free energy. The Helmholtz free energy gives

$$\left.\frac{\partial E}{\partial T}\right|_V = \left.\frac{\partial F}{\partial T}\right|_V + S + T\left.\frac{\partial S}{\partial T}\right|_V = T\left.\frac{\partial S}{\partial T}\right|_V = C_V\,, \tag{3.3}$$

the usual relation we use for definition of constant volume specific heat.

The remaining two derivatives are already within the Helmholtz free energy framework and are usually not further reduced. They are related to the isothermal bulk modulus and the thermal expansion coefficient.

As discussed above, an important quantity in a hydro-code is the sound speed. Any EOS module must be able to provide values for the sound speed for use by the hydro-code. Thus, the definition in Equation 2.24 is used to derive a formula relating the speed of sound to the four thermodynamic derivatives usually available in an EOS module, listed in Equation 3.1.

The sound speed is related to the second derivative of a thermodynamic potential, and in the derivation we will need to make diligent use of the chain rule. For the derivative, we need $P(V, S)$, but from the Helmholtz framework we have $P(V, T)$. We use

$$P(V, T) = P(V, T(V, S))\,, \tag{3.4}$$

which gives

$$\left.\frac{\partial P}{\partial V}\right|_S = \left.\frac{\partial P}{\partial V}\right|_T + \left.\frac{\partial P}{\partial T}\right|_V \left.\frac{\partial T}{\partial V}\right|_S\,. \tag{3.5}$$

The last derivative needs to be further reduced, using the Maxwell relation in Equation 2.3, the chain rule, and the equation for C_V derived in Equation 3.3:

$$-\left.\frac{\partial T}{\partial V}\right|_S = \left.\frac{\partial P}{\partial S}\right|_V = \left.\frac{\partial P}{\partial T}\right|_V \left.\frac{\partial T}{\partial S}\right|_V = \frac{\left.\frac{\partial P}{\partial T}\right|_V}{\left.\frac{\partial S}{\partial T}\right|_V} = T\,\frac{\left.\frac{\partial P}{\partial T}\right|_V}{\left.\frac{\partial E}{\partial T}\right|_V}\,. \tag{3.6}$$

Putting it all together gives the sound speed written in terms of quantities available from an EOS package:

$$c^2 = -V^2\left.\frac{\partial P}{\partial V}\right|_T + T\,V^2\,\frac{\left(\left.\frac{\partial P}{\partial T}\right|_V\right)^2}{\left.\frac{\partial E}{\partial T}\right|_V}\,. \tag{3.7}$$

Note that this equation also gives a connection between the isothermal and isentropic bulk moduli.

The last quantity used in the internal energy framework that might need to be translated to a Helmholtz picture is the Grüneisen parameter, Γ, defined in Equation 2.3. Note that the specific heat at constant volume, C_V, is directly defined in both frameworks. With straightforward use of the chain rule, or directly from Equation 3.6, we have:

$$\Gamma = \frac{V}{T}\left.\frac{\partial P}{\partial S}\right|_V = V\,\frac{\left.\frac{\partial P}{\partial T}\right|_V}{\left.\frac{\partial E}{\partial T}\right|_V}\,. \tag{3.8}$$

Rearranging and using definitions, we have

$$\Gamma\rho = \frac{\alpha\, B_T}{C_V}\,, \tag{3.9}$$

which relates two very common approximations made in analytical EOS models, that of constant $\Gamma\rho$ and C_V (Mie-Grüneisen EOS model) to that of constant αB_T and C_V (temperature amended Vinet EOS, see Equation (4.4) in Reference 3).

Phase transitions in hydro-codes: Internal energy vs Gibbs and Helmholtz free energies

Phase transition models, using the Gibbs free energy framework, implemented in hydro-codes, using the internal energy framework, need temperature derivatives along isobars and pressure derivatives along isotherms of various quantities (such as the volume and internal energy). In addition we still need to have information from the EOS package for determining explicit values for these quantities. For each phase we need

$$\left.\frac{\partial E}{\partial P}\right|_T, \left.\frac{\partial E}{\partial T}\right|_P, \left.\frac{\partial V}{\partial P}\right|_T, \left.\frac{\partial V}{\partial T}\right|_P. \tag{3.10}$$

Note that in phase transitions only derivatives with respect to intensive variables are well defined. This is the reason we replace the pressure with the volume among the two principal quantities compared to the derivatives in Equation 3.1.

Using $E = G - PV + TS$ we get

$$\left.\frac{\partial E}{\partial P}\right|_T = \left.\frac{\partial G}{\partial P}\right|_T - V - P\left.\frac{\partial V}{\partial P}\right|_T + T\left.\frac{\partial S}{\partial P}\right|_T = -P\left.\frac{\partial V}{\partial P}\right|_T - T\left.\frac{\partial V}{\partial T}\right|_P. \tag{3.11}$$

Again, we note that we only have three independent derivatives in Equation 3.10. In the same way we get

$$\left.\frac{\partial E}{\partial T}\right|_P = T\left.\frac{\partial S}{\partial T}\right|_P - P\left.\frac{\partial V}{\partial T}\right|_P. \tag{3.12}$$

We now need to relate the three Gibbs free energy framework derivatives

$$\left.\frac{\partial S}{\partial T}\right|_P, \left.\frac{\partial V}{\partial P}\right|_T, \left.\frac{\partial V}{\partial T}\right|_P, \tag{3.13}$$

to Helmholtz free energy quantities, or rather, to the derivatives in Equation 3.1.

By inverting we have

$$\left.\frac{\partial V}{\partial P}\right|_T = \frac{1}{\left.\frac{\partial P}{\partial V}\right|_T}. \tag{3.14}$$

Maxwell relations (or the cyclic rule for derivatives) and the chain rule give

$$\left.\frac{\partial V}{\partial T}\right|_P = -\left.\frac{\partial S}{\partial P}\right|_T = -\left.\frac{\partial S}{\partial V}\right|_T \left.\frac{\partial V}{\partial P}\right|_T = -\frac{\left.\frac{\partial P}{\partial T}\right|_V}{\left.\frac{\partial P}{\partial V}\right|_T} \,. \tag{3.15}$$

The last derivative is slightly more complicated and, again, we use $S(T,P) = S(T, V(P,T))$ to get

$$\left.\frac{\partial S}{\partial T}\right|_P = \left.\frac{\partial S}{\partial T}\right|_V + \left.\frac{\partial S}{\partial V}\right|_T \left.\frac{\partial V}{\partial T}\right|_P = \frac{1}{T}\left.\frac{\partial E}{\partial T}\right|_V - \left.\frac{\partial P}{\partial T}\right|_V \frac{\left.\frac{\partial P}{\partial T}\right|_V}{\left.\frac{\partial P}{\partial V}\right|_T} \,, \tag{3.16}$$

where we have also used a Maxwell relation and previously derived relations. The final results for the remaining hydro-code derivatives for phase transitions are

$$\left.\frac{\partial E}{\partial P}\right|_T = \left.\frac{\partial E}{\partial V}\right|_T \left.\frac{\partial V}{\partial P}\right|_T = \frac{\left.\frac{\partial E}{\partial V}\right|_T}{\left.\frac{\partial P}{\partial V}\right|_T} \tag{3.17}$$

$$\left.\frac{\partial E}{\partial T}\right|_P = T\left.\frac{\partial S}{\partial T}\right|_V + \left.\frac{\partial V}{\partial T}\right|_P \left(T\left.\frac{\partial S}{\partial V}\right|_T - P\right) = \left.\frac{\partial E}{\partial T}\right|_V - \frac{\left.\frac{\partial P}{\partial T}\right|_V}{\left.\frac{\partial P}{\partial V}\right|_T}\left.\frac{\partial E}{\partial V}\right|_T \,, \tag{3.18}$$

where we have used the easier path of the chain rule, instead of Equation 3.11, for the first equation

Thermodynamic derivatives for mixed phases

While the individual EOS models give values for the Helmholtz free energy derivatives and the sound speed for the individual phases, we have to derive the corresponding derivatives for a volume element in the continuum simulation with several phases present simultaneously. The internal energy and volume in an element with N phases, each with mole fraction $0 \leq \lambda_i \leq 1$, are

$$E = \sum_{i=1}^{N} \lambda_i E_i \quad \text{and} \quad V = \sum_{i=1}^{N} \lambda_i V_i \,, \tag{3.19}$$

where

$$\sum_{i=1}^{N} \lambda_i = 1 \,. \tag{3.20}$$

From this definition of internal energy and volume for the mixed phase, it is straightforward to obtain the derivatives in Equation 3.10:

$$\left.\frac{\partial E}{\partial P}\right|_T = \sum_{i=1}^{N} \lambda_i \left.\frac{\partial E_i}{\partial P}\right|_T \tag{3.21}$$

$$\left.\frac{\partial E}{\partial T}\right|_P = \sum_{i=1}^{N} \lambda_i \left.\frac{\partial E_i}{\partial T}\right|_P \tag{3.22}$$

$$\left.\frac{\partial V}{\partial P}\right|_T = \sum_{i=1}^{N} \lambda_i \left.\frac{\partial V_i}{\partial P}\right|_T \tag{3.23}$$

$$\left.\frac{\partial V}{\partial T}\right|_P = \sum_{i=1}^{N} \lambda_i \left.\frac{\partial V_i}{\partial T}\right|_P . \tag{3.24}$$

The relations in Equations 3.14, 3.15, 3.17 and 3.18 can be used for the Helmholtz free energy related quantities in Equation 3.1, since, for example, using Equation 3.23, we have

$$\left.\frac{\partial V}{\partial P}\right|_T = \frac{1}{\left.\frac{\partial P}{\partial V}\right|_T} = \sum_{i=1}^{N} \lambda_i \frac{1}{\left.\frac{\partial P}{\partial V_i}\right|_T} , \tag{3.25}$$

so that

$$\left.\frac{\partial P}{\partial V}\right|_T = \frac{1}{\sum_{i=1}^{N} \lambda_i \frac{1}{\left.\frac{\partial P}{\partial V_i}\right|_T}} . \tag{3.26}$$

The remaining relations give:

$$-\left.\frac{\partial V}{\partial T}\right|_P = \frac{\left.\frac{\partial P}{\partial T}\right|_V}{\left.\frac{\partial P}{\partial V}\right|_T} = \sum_{i=1}^{N} \lambda_i \frac{\left.\frac{\partial P}{\partial T}\right|_{V_i}}{\left.\frac{\partial P}{\partial V_i}\right|_T} \tag{3.27}$$

$$\left.\frac{\partial E}{\partial P}\right|_T = \frac{\left.\frac{\partial E}{\partial V}\right|_T}{\left.\frac{\partial P}{\partial V}\right|_T} = \sum_{i=1}^{N} \lambda_i \frac{\left.\frac{\partial E_i}{\partial V_i}\right|_T}{\left.\frac{\partial P}{\partial V_i}\right|_T} \tag{3.28}$$

$$\left.\frac{\partial E}{\partial T}\right|_P = \left.\frac{\partial E}{\partial T}\right|_V - \frac{\left.\frac{\partial P}{\partial T}\right|_V \left.\frac{\partial E}{\partial V}\right|_T}{\left.\frac{\partial P}{\partial V}\right|_T} = \sum_{i=1}^{N} \lambda_i \left(\left.\frac{\partial E_i}{\partial T}\right|_{V_i} - \frac{\left.\frac{\partial P}{\partial T}\right|_{V_i} \left.\frac{\partial E_i}{\partial V_i}\right|_T}{\left.\frac{\partial P}{\partial V_i}\right|_T} \right) , \tag{3.29}$$

so that the three remaining Helmholtz free energy related quantities in Equation 3.1 are

$$\left.\frac{\partial P}{\partial T}\right|_V = \left.\frac{\partial P}{\partial V}\right|_T \sum_{i=1}^{N} \lambda_i \frac{\left.\frac{\partial P}{\partial T}\right|_{V_i}}{\left.\frac{\partial P}{\partial V_i}\right|_T} \tag{3.30}$$

$$\left.\frac{\partial E}{\partial V}\right|_T = \left.\frac{\partial P}{\partial V}\right|_T \sum_{i=1}^{N} \lambda_i \frac{\left.\frac{\partial E_i}{\partial V_i}\right|_T}{\left.\frac{\partial P}{\partial V_i}\right|_T} \tag{3.31}$$

$$\left.\frac{\partial E}{\partial T}\right|_V = \frac{\left.\frac{\partial P}{\partial T}\right|_V \left.\frac{\partial E}{\partial V}\right|_T}{\left.\frac{\partial P}{\partial V}\right|_T} + \sum_{i=1}^{N} \lambda_i \left(\left.\frac{\partial E_i}{\partial T}\right|_{V_i} - \frac{\left.\frac{\partial P}{\partial T}\right|_{V_i} \left.\frac{\partial E_i}{\partial V_i}\right|_T}{\left.\frac{\partial P}{\partial V_i}\right|_T} \right) . \tag{3.32}$$

Note, in particular, that highly nontrivial relation for the constant volume specific heat for a mixture of phases given in the last equation.

By using the previously derived relation between the sound speed and the EOS quantities, Equation 3.7, we can get the sound speed for the mixed phase. However, it is illustrative to derive a relation between the sound speed of the separate phases and the total sound speed.

As seen in Equation 2.24, the sound speed is related to the volume derivative of the pressure along an isentrope, but only derivatives along isotherms and isobars are well defined in a mixed phase. We will need to find a relation between the sound speed and derivatives with respect to temperature along isobars, and/or derivatives with respect to pressure along isotherms.

The Maxwell's relation derived from enthalpy, Equation 2.19, gives a translation from derivatives along isentropes to derivatives along isobars. By inverting this relation,

$$\left.\frac{\partial P}{\partial T}\right|_S = \left.\frac{\partial S}{\partial V}\right|_P , \tag{3.33}$$

and noting that we need a derivative with respect to temperature to go with the isobar on the right hand side in order to have a well defined quantity in a mixed phase, we get

$$\left.\frac{\partial S}{\partial T}\right|_P = \left.\frac{\partial S}{\partial V}\right|_P \left.\frac{\partial V}{\partial T}\right|_P = \left.\frac{\partial P}{\partial T}\right|_S \left.\frac{\partial V}{\partial T}\right|_P = \left.\frac{\partial P}{\partial V}\right|_S \left.\frac{\partial V}{\partial T}\right|_S \left.\frac{\partial V}{\partial T}\right|_P . \tag{3.34}$$

Since entropy is an extensive variable we have a similar relation for it in a mixed phase as we have for the internal energy and volume:

$$S = \sum_{i=1}^{N} \lambda_i S_i , \tag{3.35}$$

which we can now use to get

$$\left.\frac{\partial S}{\partial T}\right|_P = \sum_{i=1}^{N} \lambda_i \left.\frac{\partial S_i}{\partial T}\right|_P . \tag{3.36}$$

The two last terms in Equation 3.34 need to be written as derivatives with respect to volume along isotherms and/or derivatives with respect to temperature along isochores, quantities that we can get from our EOS. We proceed by using the already derived relations in Equations 3.6 (inverted) and 3.15 to obtain

$$T\,\frac{\partial S}{\partial T}\bigg|_P = \frac{\partial P}{\partial V}\bigg|_S \frac{\frac{\partial E}{\partial T}\big|_V}{\frac{\partial P}{\partial V}\big|_T}\,. \tag{3.37}$$

This results in

$$c^2\,\frac{\frac{\partial E}{\partial T}\big|_V}{V^2\,\frac{\partial P}{\partial V}\big|_T} = \sum_{i=1}^{N} \lambda_i\, c_i^2\, \frac{\frac{\partial E_i}{\partial T}\big|_{V_i}}{V_i^2\,\frac{\partial P}{\partial V_i}\Big|_T}\,. \tag{3.38}$$

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Chapter 4

Summary

Each of four different thermodynamic potentials contain all necessary quantities for describing the thermodynamic state of a system. However, depending on the situation, one or the other of the thermodynamic potentials can be more convenient to use, since each has its own specific set of natural variables:

- The internal energy has entropy and volume as natural variables, $E(S, V)$.
- The Helmholtz free energy, $F = E - TS$, has volume and temperature as natural variables, $F(V, T)$.
- The Gibbs free energy, $G = F + PV$, has temperature and pressure as natural variables, $G(T, P)$.
- The enthalpy, $H = G - TS$ has pressure and entropy as natural variables, $H(P, S)$.

Complications arise, however, when a situation requires connections between two, or more, different frameworks. An example is when a hydro-code, with a natural framework of internal energy, needs an equation of state, with a natural framework of Helmholtz free energy. In those situations relations between thermodynamic derivatives within different frameworks need to be derived. The key to successful derivations is to use

- *Maxwell relations* (Eqns 2.3, 2.8, 2.14, and 2.19), derived from that the second order derivative of a thermodynamic potential with respect to both its natural variables is independent of the order that the derivatives are taken, and
- diligent use of the chain rule (see, for example, Eqns 3.5 and 3.16).

Several useful relations are derived in Chapter 3. If other relations are needed, they can be derived according to the same methodology, or they can be looked up in Rebecca Brannon's excellent write-up in Reference 2.

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References

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[4] Ya. B. Zel′dovich and Yu. P. Raizer. *Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena.* Dover Publications, Mineola, NY, 2002.

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