Review of Thermodynamics. 3: Second-Order Quantities and Relationships

Maxwell Relations

• *Idea:* Each thermodynamic potential gives rise to several identities among its second derivatives, known as Maxwell relations, which express the integrability of the fundamental identity of thermodynamics for that potential, or equivalently the fact that the potential really is a thermodynamical state function.

• *Example:* From the fundamental identity of thermodynamics written in terms of the Helmholtz free energy, $dF = -S\,dT - p\,dV + ...$, the fact that dF really is the differential of a state function implies that

$$\frac{\partial}{\partial V}\frac{\partial F}{\partial T} = \frac{\partial}{\partial T}\frac{\partial F}{\partial V}, \qquad \text{or} \qquad \left.\frac{\partial S}{\partial V}\right|_{T,N} = \left.\frac{\partial p}{\partial T}\right|_{V,N}.$$

• *Other Maxwell relations:* From the same identity, if $F = F(T, V, N)$ we get two more relations. Other potentials and/or pairs of variables can be used to obtain additional relations. For example, from the Gibbs free energy and the identity $dG = -S\,dT + V\,dp + \mu\,dN$, we get three relations, including

$$\frac{\partial}{\partial p}\frac{\partial G}{\partial T} = \frac{\partial}{\partial T}\frac{\partial G}{\partial p}, \qquad \text{or} \qquad \left.\frac{\partial S}{\partial p}\right|_{T,N} = -\left.\frac{\partial V}{\partial T}\right|_{p,N}.$$

• *Applications:* Some measurable quantities, response functions such as heat capacities and compressibilities, are second-order thermodynamical quantities (i.e., their definitions contain derivatives up to second order of thermodynamic potentials), and the Maxwell relations provide useful equations among them.

Heat Capacities

• *Definitions:* A heat capacity is a response function expressing how much a system's temperature changes when heat is transferred to it, or equivalently how much δQ is needed to obtain a given dT. The general definition is $C = \delta Q/dT$, where for any reversible transformation $\delta Q = T\,dS$, but the value of this quantity depends on the details of the transformation. The two most common types of heat capacities are

$$C_V := T\left.\frac{\partial S}{\partial T}\right|_{V,N} = -T\left.\frac{\partial^2 F}{\partial T^2}\right|_{V,N} \text{ or } \left.\frac{\partial E}{\partial T}\right|_{V,N}, \qquad C_p := T\left.\frac{\partial S}{\partial T}\right|_{p,N} = -T\left.\frac{\partial^2 G}{\partial T^2}\right|_{p,N} \text{ or } \left.\frac{\partial H}{\partial T}\right|_{p,N}.$$

• *Relationship between heat capacities:* In general, $C_p > C_V$, because when the system is heated at constant p work is done to increase the volume, and because the internal energy may depend on V. In particular, from $\delta Q = dE + p\,dV$ and $dE = \partial E/\partial T|_V\,dT + \partial E/\partial V|_T\,dV = C_V\,dT + \partial E/\partial V|_T\,dV$ we get [Schwabl §3.2]

$$C_p = C_V + \left(p + \left.\frac{\partial E}{\partial V}\right|_{T,N}\right)\left.\frac{\partial V}{\partial T}\right|_{p,N}.$$

A more explicit relation will be derived below, involving the compressibility and thermal coefficient.

• *Third law revisited:* For a reversible transformation $dS = \delta Q/T$, and if V is constant $dS = C_V\,dT/T$, so

$$S(T_f, V, N) = S(T_i, V, N) + \int_{T_i}^{T_f} \frac{C_V\,dT}{T},$$

and if the entropy vanishes, or more generally approaches a finite constant, as $T \to 0$, this implies $C_V \to 0$.

Compressibilities

• *Definitions:* Compressibilities are response functions expressing how a systems's volume responds to a change in the applied pressure. The isothermal and adiabatic compressibilities are defined respectively as

$$\kappa_T := -\frac{1}{V}\left.\frac{\partial V}{\partial p}\right|_{T,N} = -\frac{1}{V}\left.\frac{\partial^2 G}{\partial p^2}\right|_{T,N}, \qquad \kappa_S := -\frac{1}{V}\left.\frac{\partial V}{\partial p}\right|_{S,N} = -\frac{1}{V}\left.\frac{\partial^2 H}{\partial^2 p}\right|_{S,N}.$$

• *Application:* The speed of sound in a material of density ρ and adiabatic compressibility κ_S is $c = 1/\sqrt{\rho\kappa_S}$.

Thermal Coefficients and Other Useful Relationships

• *Definitions:* Thermal coefficients characterize the response of the volume and pressure of a system to a change in temperature. The thermal expansion and thermal pressure coefficients are, respectively,

$$\alpha := \frac{1}{V}\frac{\partial V}{\partial T}\Big|_{p,N}, \qquad \beta := \frac{1}{p}\frac{\partial p}{\partial T}\Big|_{V,N}.$$

• *Relationship between heat capacities:* We can now express the relationship between C_p and C_V in terms of measurable quantities. Starting with the general fact that $S = S(T,V)$,

$$dS = \frac{\partial S}{\partial T}\Big|_{V,N} dT + \frac{\partial S}{\partial V}\Big|_{T,N} dV, \qquad \text{or} \qquad \frac{C_p}{T} = \frac{C_V}{T} + \frac{\partial p}{\partial T}\Big|_{V,N}\frac{\partial V}{\partial T}\Big|_{p,N},$$

where we have divided by dT keeping p constant, and used one of the Maxwell relations. Finally, using the fact that for any three variables x, y, z with the functional dependence $z = z(x,y)$ we have the "triple-product rule" $(\partial x/\partial y)_z = -(\partial x/\partial z)_y (\partial z/\partial y)_x$,* and the above definitions [with $x \leftrightarrow p$, $y \leftrightarrow T$, $z \leftrightarrow V$],

$$C_p = C_V + \frac{TV}{\kappa_T}\alpha^2.$$

• *Compressibilities and adiabatic constant:* Using the Maxwell relations, one can similarly derive that

$$\kappa_T = \kappa_S + \frac{TV}{C_p}\alpha^2,$$

that the quantity defined by $\gamma := \kappa_T/\kappa_S$ is, in the case of an ideal gas, the constant appearing in the adiabatic transformation law $pV^\gamma = \text{const}$ (adiabatic constant or index), and that

$$\frac{C_p}{C_V} = \frac{\kappa_T}{\kappa_S}.$$

Other Response Functions

• *Magnetic material:* In an applied magnetic field $\vec{B}$, the fundamental identity and the susceptibility are

$$dE = T\,dS - \vec{M}\cdot d\vec{B} + \dots, \qquad \chi := \partial M/\partial B,$$

and characterizes the response of the material's magnetization to a change in the applied field. As with other response functions, one must specify in the definition which quantities are kept constant in the process.

Stability Conditions on Second-Order Quantities

• *Idea:* The signs in the definitions of these response functions are chosen so that their values for most common thermodynamical systems are positive. Negative values would then be associated with instabilities of the systems: It follows from simple physical arguments that a system with a negative heat capacity $C < 0$ cannot be in stable thermal equilibrium with its environment, and one with a negative compressibility $\kappa < 0$ cannot be in stable mechanical equilibrium. (One can also relate these properties to stability criteria expressed as maximum and minimum conditions on thermodynamic potentials—see Chandler §2.2).

• *Remark:* There exist physical systems with negative heat capacities (one example are black holes, but there are less exotic ones), and metamaterials with negative compressibilities. Those systems are thermodynamically unstable, although their instability time scales may vary considerably and the ones with longer time scales may be physically relevant.

Reading

• *Kennett:* Appendix B, Section B.4.

• *Short summaries:* Chandler, §§ 1.6, 2.2; Halley, 2nd half of Ch 3; Kardar, §§ 1.8, 1.9; Mattis & Swendsen, §§ 3.3, 3.5; Plischke & Bergersen, §§ 1.5–1.6; Reichl, §§ 3.6, 3.7; Reif, §§ 5.5–5.7; Schwabl, §§ 3.1-3.3.

• *Good undergraduate-level textbooks with more complete treatments:* Schroeder 2000; Huang 2010.

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* Derivation: Start from a function $z = z(x,y)$, write down its variation $dz = (\partial z/\partial x)_y\,dx + (\partial z/\partial y)_x\,dy$, apply to a variation in which z does not change, and divide by dy.