Maxwell Relations

• *Idea:* Using basic identities for functions of several variables, each thermodynamic potential gives rise to several identities among derivatives of the first-order variables, known as Maxwell relations, which express the integrability of the first law of thermodynamics.
• *Example:* From $\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V + ...$, and the fact that F is a function of state, we get

$$\frac{\partial S}{\partial V}\Big|_{T,N} = \frac{\partial p}{\partial T}\Big|_{V,N} .$$

• *Other Maxwell relations:*

Heat Capacities

• *Definitions:* The heat capacity for a system is generally defined as $C = \mathrm{d}Q/\mathrm{d}T$; More specifically, using the fact that in a reversible transformation $\mathrm{d}Q = T\mathrm{d}S$, we define the heat capacities

$$C_\mathrm{v} = T\,\frac{\partial S}{\partial T}\Big|_{V,N} = -T\,\frac{\partial^2 F}{\partial T^2}\Big|_{V,N} , \qquad C_\mathrm{p} = T\,\frac{\partial S}{\partial T}\Big|_{p,N} = -T\,\frac{\partial^2 G}{\partial T^2}\Big|_{p,N} .$$

• *Relationship between heat capacities:* Starting with the general fact that $S = S(T, V)$,

$$\mathrm{d}S = \frac{\partial S}{\partial T}\Big|_{V,N}\mathrm{d}T + \frac{\partial S}{\partial V}\Big|_{T,N}\mathrm{d}V , \qquad \text{or} \qquad \frac{C_\mathrm{p}}{T} = \frac{C_\mathrm{v}}{T} + \frac{\partial p}{\partial T}\Big|_{V,N}\frac{\partial V}{\partial T}\Big|_{p,N} ,$$

where we have divided by $\mathrm{d}T$ keeping p constant, and used one of the Maxwell relations. Finally, using the general fact that $(\partial x/\partial y)_z = -(\partial x/\partial z)_y\,(\partial z/\partial y)_x$,* and the above definitions,

$$C_\mathrm{p} = C_\mathrm{v} + TV\alpha^2/\kappa_\mathrm{t} .$$

• *Heat capacities and adiabatic coefficient:* For a gas of particles with f degrees of freedom, derive

$$\gamma = \frac{C_\mathrm{p}}{C_\mathrm{v}} = 1 + \frac{2}{f} .$$

Other Useful Second-Order Thermodynamic Quantities

• *For a fluid:* Other quantities of interest are the isothermal compressibility, the thermal expansion coefficient, and the thermal pressure coefficient, defined respectively as

$$\kappa_\mathrm{t} := -\frac{1}{V}\,\frac{\partial V}{\partial p}\Big|_{T,N} = -\frac{1}{V}\,\frac{\partial^2 G}{\partial p^2}\Big|_{T,N} , \qquad \alpha := \frac{1}{V}\,\frac{\partial V}{\partial T}\Big|_{p,N} , \qquad ...$$

• *For a magnetic material:* The magnetic susceptibility, defined as

$$\chi := \frac{\partial M}{\partial B} .$$

Stability Conditions on Second-Order Quantities

Relevant Sections: PHY 731; Chandler; Halley; Reif; Schwabl, §3.1-3.3.

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