

may be written as

$$p = -\left(\frac{\partial U}{\partial V}\right)_\tau + \tau \left(\frac{\partial \sigma}{\partial V}\right)_\tau, \quad (50)$$

by use of $F \equiv U - \tau\sigma$. The two terms on the right-hand side of (50) represent what we may call the energy pressure and the entropy pressure. The energy pressure $-(\partial U/\partial V)_\tau$ is dominant in most solids and the entropy pressure $\tau(\partial\sigma/\partial V)_\tau$ is dominant in gases and in elastic polymers such as rubber (Problem 10). The entropy contribution is testimony of the importance of the entropy: the naive feeling from simple mechanics that $-dU/dV$ must tell everything about the pressure is seriously incomplete for a process at constant temperature, because the entropy can change in response to the volume change even if the energy is independent of volume, as for an ideal gas at constant temperature.

Maxwell relation. We can now derive one of a group of useful thermodynamic relations called Maxwell relations. Form the cross-derivatives $\partial^2 F/\partial V \partial \tau$ and $\partial^2 F/\partial \tau \partial V$, which must be equal to each other. It follows from (49) that

$$(\partial\sigma/\partial V)_\tau = (\partial p/\partial \tau)_V, \quad (51)$$

a relation that is not at all obvious. Other Maxwell relations will be derived later at appropriate points, by similar arguments. The methodology of obtaining thermodynamic relations is discussed by R. Gilmore, J. Chem. Phys. **75**, 5964 (1981).

Calculation of F from Z

Because $F \equiv U - \tau\sigma$ and $\sigma = -(\partial F/\partial \tau)_V$, we have the differential equation

$$F = U + \tau(\partial F/\partial \tau)_V, \quad \text{or} \quad -\tau^2 \partial(F/\tau)/\partial \tau = U. \quad (52)$$

We show that this equation is satisfied by

$$F/\tau = -\log Z, \quad (53)$$

where Z is the partition function. On substitution,

$$\partial(F/\tau)/\partial \tau = -\partial \log Z/\partial \tau = -U/\tau^2 \quad (54)$$