Thus in the magnetic field B the thermal equilibrium value of the spin excess $2s$ is given by

$$\frac{N + \langle 2s \rangle}{N - \langle 2s \rangle} = \exp(2mB/\tau); \qquad \langle 2s \rangle = N\left(\frac{\exp(2mB/\tau) - 1}{\exp(2mB/\tau) + 1}\right), \tag{44}$$

or, on dividing numerator and denominator by $\exp(mB/\tau)$,

$$\langle 2s \rangle = N \tanh(mB/\tau). \tag{45}$$

The magnetization M is the magnetic moment per unit volume. If n is the number of spins per unit volume, the magnetization in thermal equilibrium in the magnetic field is

$$M = \langle 2s \rangle m/V = nm \tanh(mB/\tau). \tag{46}$$

The free energy of the system in equilibrium can be obtained by substituting (45) in (42). It is easier, however, to obtain F directly from the partition function for one magnet:

$$Z = \exp(mB/\tau) + \exp(-mB/\tau) = 2\cosh(mB/\tau). \tag{47}$$

Now use the relation $F = -\tau \log Z$ as derived below. Multiply by N to obtain the result for N magnets. (The magnetization is derived more simply by the method of Problem 2.)

Differential Relations

The differential of F is

$$dF = dU - \tau d\sigma - \sigma d\tau ,$$

or, with use of the thermodynamic identity (34a),

$$dF = -\sigma d\tau - pdV , \tag{48}$$

for which

$$\boxed{\left(\frac{\partial F}{\partial \tau}\right)_V = -\sigma; \qquad \left(\frac{\partial F}{\partial V}\right)_\tau = -p.} \tag{49}$$

These relations are widely used.

The free energy F in the result $p = -(\partial F/\partial V)_\tau$ acts as the effective energy for an *isothermal* change of volume; contrast this result with (26). The result