order to make a surface, and γ tells you how much energy you need to form unit area of surface (which gives an estimate of the size of the intermolecular forces).

We can write the first law of thermodynamics for our surface of area A as

$$\mathrm{d}U = T\,\mathrm{d}S + \gamma\,\mathrm{d}A \tag{17.20}$$

and similarly changes in the Helmholtz function can be written

$$\mathrm{d}F = -S\,\mathrm{d}T + \gamma\,\mathrm{d}A, \tag{17.21}$$

which yields the Maxwell relation

$$\left(\frac{\partial S}{\partial A}\right)_T = -\left(\frac{\partial \gamma}{\partial T}\right)_A. \tag{17.22}$$

Equation 17.20 implies that

$$\left(\frac{\partial U}{\partial A}\right)_T = T\left(\frac{\partial S}{\partial A}\right)_T + \gamma, \tag{17.23}$$

and hence using eqn 17.22, we have that

$$\left(\frac{\partial U}{\partial A}\right)_T = \gamma - T\left(\frac{\partial \gamma}{\partial T}\right)_A, \tag{17.24}$$

the sum of a positive term expressing the energy going into a surface by work and a negative term expressing the heat flow into the surface due to an isothermal change of area. Usually, the surface tension has a temperature dependence as shown in Fig. 17.5, and hence $(\partial\gamma/\partial T)_A < 0$, so in fact both terms contribute a positive amount.

Heat ΔQ is given by

$$\Delta Q = T\left(\frac{\partial S}{\partial A}\right)_T \Delta A = -T\Delta A\left(\frac{\partial \gamma}{\partial T}\right)_A > 0, \tag{17.25}$$

and this is absorbed on isothermally stretching a surface to increase its area by ΔA. This quantity is positive and so heat really is absorbed. Since $\left(\frac{\partial S}{\partial A}\right)_T$ is positive, this shows that the surface has an additional entropy compared to the bulk, in addition to costing extra energy.
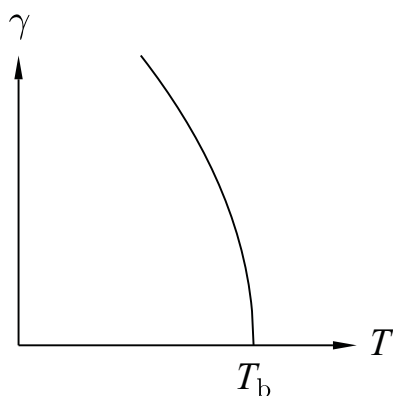

Fig. 17.5 Schematic diagram of the surface tension γ of a liquid as a function of temperature. Since γ must vanish at the boiling temperature T_{b}, we expect that $(\partial\gamma/\partial T)_A < 0$.

17.3 Paramagnetism

Consider a system of magnetic moments arranged in a lattice at temperature T. We assume that the magnetic moments cannot interact with each other. If the application of a magnetic field causes the magnetic moments to line up, the system is said to exhibit **paramagnetism**. The equivalent formulation of the first law of thermodynamics for a paramagnet is

$$\mathrm{d}U = T\,\mathrm{d}S + B\,\mathrm{d}m, \tag{17.26}$$

where m is the **magnetic moment** and B is the **magnetic field**.[4] The

[4]B is often known as the **magnetic flux density** or the **magnetic induction**, but following common usage, we refer to B as the magnetic field; see Blundell (2001). The magnetic field H (often called the **magnetic field strength**) is related to B and the magnetization M by

$$B = \mu_0(H + M).$$