rapidly $\Omega(E)$ increases with E, the shaper this maximum becomes. Thus we arrive again at the conclusions of Sec. 3·7. We emphasize, however, that (6·2·9) is valid no matter how small A is. It may even be a system of atomic size, provided that it can be treated as a distinguishable system satisfying the additivity of energy (6·2·1).

Once the probability distribution (6·2·7) is known, various mean values can readily be computed. For example, let y be any quantity assuming the value y_r in state r of the system A. Then

$$\bar{y} = \frac{\sum_r e^{-\beta E_r} y_r}{\sum_r e^{-\beta E_r}} \tag{6·2·10}$$

where the summation is over all states r of the system A.

6 · 3 *Simple applications of the canonical distribution*

The canonical distribution (6·2·7) yields a host of conclusions. Here we mention only a few illustrative applications where the canonical distribution leads immediately to physically very important results. Most of these will be discussed more fully in Chapter 7.

Paramagnetism Consider a substance which contains N_0 magnetic atoms per unit volume and which is placed in an external magnetic field $\boldsymbol{H}$. Assume that each atom has spin $\frac{1}{2}$ (corresponding to one unpaired electron) and an intrinsic magnetic moment μ. In a quantum-mechanical description the magnetic moment of each atom can then point either parallel or antiparallel to the external field $\boldsymbol{H}$. If the substance is at absolute temperature T, what is the mean magnetic moment $\bar{\mu}_H$ (in the direction of $\boldsymbol{H}$) of such an atom? We assume that each atom interacts only weakly with the other atoms and with the other degrees of freedom of the substance. It is then permissible to focus attention on a single atom as the small system under consideration and to regard all the other atoms and other degrees of freedom as constituting a heat reservoir.*

Each atom can be in two possible states: the state $(+)$ where its spin points up (i.e., parallel to $\boldsymbol{H}$) and the state $(-)$ where its spin points down (i.e., antiparallel to $\boldsymbol{H}$). Let us discuss these states in turn.

In the $(+)$ state, the atomic magnetic moment $\boldsymbol{\mu}$ is parallel to $\boldsymbol{H}$ so that $\mu_H = \mu$. The corresponding magnetic energy of the atom is then $\epsilon_+ = -\mu H$.

---

* This assumes that it is possible to identify a single atom unambiguously, an assumption which is justified if the atoms are localized at definite lattice sites of a solid or if they form a dilute gas where the atoms are widely separated. In a concentrated gas the assumption might break down. It would then be necessary to adopt a point of view (which is always permissible, although more complicated) which considers the *entire* gas of atoms as a small microscopic system in contact with a heat reservoir provided by other degrees of freedom.

The probability of finding the atom in this state is thus

$$P_+ = C\,e^{-\beta\epsilon_+} = C\,e^{\beta\mu H} \tag{6·3·1}$$

where C is a constant of proportionality and $\beta = (kT)^{-1}$. This is the state of lower energy (if μ is positive) and is thus the state in which the atom is more likely to be found.

In the $(-)$ state, $\boldsymbol{\mu}$ is antiparallel to $\boldsymbol{H}$ so that $\mu_H = -\mu$. The corresponding energy of the atom is then $\epsilon_- = +\mu H$. The probability of finding the atom in this state is thus

$$P_- = C\,e^{-\beta\epsilon_-} = C\,e^{-\beta\mu H} \tag{6·3·2}$$

This is the state of higher energy (if μ is positive) and is thus the state in which the atom is less likely to be found.

Since the first state where $\boldsymbol{\mu}$ is parallel to $\boldsymbol{H}$ is more probable, it is clear that the mean magnetic moment $\bar{\mu}_H$ must point in the direction of the external field $\boldsymbol{H}$. By virtue of (6·3·1) and (6·3·2), the significant parameter in this problem is the quantity

$$y \equiv \beta\mu H = \frac{\mu H}{kT}$$

which measures the ratio of a typical magnetic energy to a typical thermal energy. It is apparent that if T is very large, i.e., if $y \ll 1$, the probability that $\boldsymbol{\mu}$ is parallel to $\boldsymbol{H}$ is almost the same as that of its being antiparallel. In this case $\boldsymbol{\mu}$ is almost completely randomly oriented so that $\bar{\mu}_H \approx 0$. On the other hand, if T is very small, i.e., if $y \gg 1$, then it is much more probable that $\boldsymbol{\mu}$ is parallel to $\boldsymbol{H}$ rather than antiparallel to it. In this case $\bar{\mu}_H \approx \mu$.

All these qualitative conclusions can readily be made quantitative by actually calculating the mean value $\bar{\mu}_H$. Thus we have

$$\bar{\mu}_H = \frac{P_+\mu + P_-(-\mu)}{P_+ + P_-} = \mu\,\frac{e^{\beta\mu H} - e^{-\beta\mu H}}{e^{\beta\mu H} + e^{-\beta\mu H}}$$

or

$$\bar{\mu}_H = \mu \tanh\frac{\mu H}{kT} \tag{6·3·3}$$

Here we have used the definition of the hyperbolic tangent

$$\tanh y \equiv \frac{e^y - e^{-y}}{e^y + e^{-y}}$$

The "magnetization" $\bar{M}_0$, or mean magnetic moment per unit volume, is then in the direction of H and is given by

$$\bar{M}_0 = N_0\bar{\mu}_H \tag{6·3·4}$$

One can easily check that $\bar{\mu}_H$ exhibits the qualitative behavior already discussed. If $y \ll 1$, then $e^y = 1 + y + \cdots$ and $e^{-y} = 1 - y + \cdots$. Hence

$$\text{for } y \ll 1, \qquad \tanh y = \frac{(1 + y + \cdots) - (1 - y - \cdots)}{2} = y$$

On the other hand, if $y \gg 1$, then $e^y \gg e^{-y}$. Hence

$$\text{for } y \gg 1, \qquad \tanh y = 1$$

Thus (6·3·3) leads to the limiting behavior that

$$\text{for } \mu H/kT \ll 1, \qquad \bar{\mu}_H = \frac{\mu^2 H}{kT} \tag{6·3·5a}$$

$$\text{for } \mu H/kT \gg 1, \qquad \bar{\mu}_H = \mu \tag{6·3·5b}$$

By (6·3·4) and (6·3·5a) it then follows that

$$\text{if } \mu H/kT \ll 1, \qquad \bar{M}_0 = \chi H \tag{6·3·6}$$

where χ is a constant of proportionality independent of H. This parameter χ is called the "magnetic susceptibility" of the substance. Equation (6·3·5a) provides an explicit expression for χ in terms of microscopic quantities, i.e.,

$$\chi = \frac{N_0 \mu^2}{kT} \tag{6·3·7}$$

The fact that $\chi \propto T^{-1}$ is known as Curie's law. On the other hand,

$$\text{if } \mu H/kT \gg 1, \qquad \bar{M}_0 \to N_0 \mu \tag{6·3·8}$$

becomes independent of H and equal to the maximum (or "saturation") magnetization which the substance can exhibit. The complete dependence of the magnetization $\bar{M}_0$ on temperature T and magnetic field H is shown in Fig. 6·3·1.

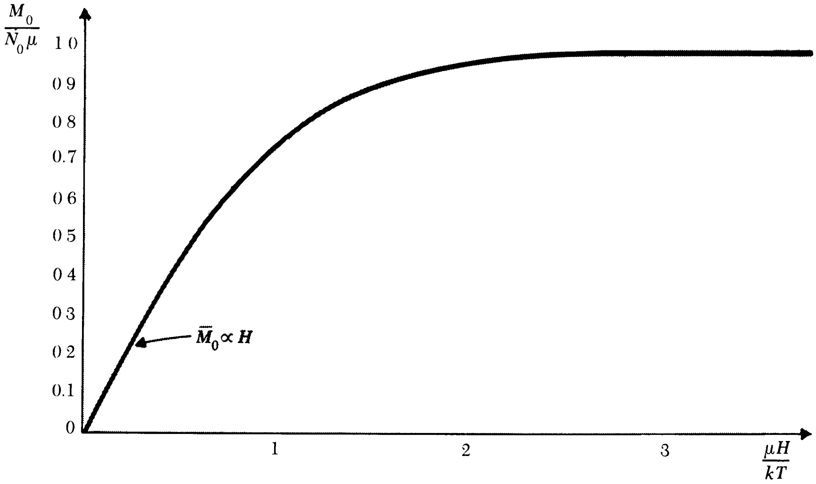

***Fig. 6·3·1** Dependence of the magnetization $\bar{M}_0$ on magnetic field H and temperature T for noninteracting magnetic atoms of spin $\frac{1}{2}$ and magnetic moment μ.*