CHAPTER 12

THERMODYNAMICS OF MAGNETIC SYSTEMS

12.1 Introduction

Thermodynamics applies to much more than just simple compressible substances. We've dealt briefly with magnetic work. In this chapter, we'll discuss in more depth the thermodynamics of materials on which magnetic work can be done.

12.2 The Simple Magnetic Substance

Magnetic fields can interact with some materials, causing work to be done on or by them. Here we consider the simplest case, when magnetic work is the only possible reversible work mode.

If a substance contains molecules or ions which have permanent magnetic dipole moments (for example, O_2 or rare-earth ions), then an external magnetic field can do work on the sample by turning these dipoles to align with the field. Such materials are known as *paramagnetic*.

A magnetic field can also do work on a substance by inducing electrical currents to flow. These currents may be macroscopic ones, like those induced in the surface layer of a perfect conductor when a magnetic field is applied, or atomic-scale ones due to slight changes in the motion of the electrons orbiting about the nuclei due to the magnetic field. In either case, materials in which currents are induced when a magnetic field is applied are called *diamagnetic*.

The net magnetic dipole moment of a sample per unit volume defines the magnetization \vec{M} . Note that \vec{M} is a vector. For the paramagnetic case, it is the vector sum of all individual magnetic dipole moments. If they point in random directions (as they do with no applied field), then their vector sum is zero and $\vec{M} = 0$. But if a field is applied so they are at least partially aligned, then there is a net magnetization pointing in the direction of the applied field. (They are not perfectly aligned since collisions with other molecules or with the lattice in a solid tend to upset the alignment.)

For diamagnetic materials, there is also a magnetization, since current loops have a magnetic moment associated with them. It may be shown that the

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magnetization of a diamagnetic material points *opposite* to the direction of the magnetic field.

All materials have some diamagnetic response, but it is usually weak. Except in extremely strong fields, most diamagnetic materials can be considered nonmagnetic. If the material contains permanent magnetic dipoles, then the paramagnetic response is usually much larger and the diamagnetism can be neglected.

Finally, the most familiar form of magnetism is *ferromagnetism*. Permanent magnets, which by definition are magnetized even in zero applied field, are made of ferromagnetic materials. Only the elements Fe, Co, Ni, and Gd exhibit ferromagnetism, and all permanent magnets contain at least one of these elements. The ferromagnetic elements have permanent magnetic dipoles, like paramagnetic materials. The difference is that the dipoles exert forces on one another which tend to lock them into alignment even without an external magnetic field. If a ferromagnetic material is heated, beyond a certain temperature the forces between dipoles are overcome, and the material becomes paramagnetic. This temperature is known as the *Curie Point*, and for iron it is 770 °C.

In general, a paramagnetic, diamagnetic, or ferromagnetic substance may have other work modes too. For example, oxygen gas is paramagnetic but also is compressible. A liquid oxygen droplet will have a surface tension, so deforming the droplet is another work mode. But in most cases, magnetic materials are solid, and reasonably incompressible. In this case, the only important work mode is magnetic work, and we may then treat the substance as a *simple magnetic substance*. This is the only case we will consider here.

When an external magnetic field is applied to a sample, the response of the sample (turning dipoles or induced currents) modifies the local value of the field within the sample. We define \vec{H} to represent the applied field which would exist without the sample, and \vec{B} to represent the true field value in the sample. The quantities \vec{B} , \vec{H} , and \vec{M} are related by ¹

$$\vec{B} = \mu_0 (\vec{H} + \vec{M}).$$
 (12.1)

The value of the field without the sample is really $\mu_0 \vec{H}$, but since μ_0 is just a constant $(4\pi \times 10^{-7} \text{ tesla-m/amp})$ we can treat \vec{H} as representing the applied magnetic field.

¹This equation depends on the unit system. The form here is for the Rationalized MKS system, which is the one used most commonly in applied science and engineering. In another unit system widely used in physics (cgs), \vec{B} and \vec{H} have the same units and equation 12.1 is replaced by $\vec{B} = \vec{H} + 4\pi \vec{M}$

We've shown previously that the work required to reversibly magnetize a magnetic substance is

$$dW = \mu_0 \vec{H} \cdot d(\vec{M}V). \tag{12.2}$$

The Gibbs equation for a simple magnetic substance may be derived by considering a reversible process in which magnetic work dW is done and heat dQ = TdS is added. Since dU = dQ + dW,

$$dU = TdS + \mu_0 \vec{H} \cdot d(\vec{M}V). \tag{12.3}$$

On a unit mass basis,

$$du = Tds + \mu_0 \vec{H} \cdot d(\vec{M}v). \tag{12.4}$$

We can simplify the notation by defining

$$\vec{m} = \mu_0 v \vec{M}. \tag{12.5}$$

Also, the magnetization is generally either parallel to \vec{H} (paramagnetic substances) or anti-parallel (diamagnetic substances). Therefore, $\vec{H} \cdot d\vec{m} = Hm$, where m < 0 in the diamagnetic case.

The magnetic Gibbs equation then becomes

$$du = Tds + Hdm. (12.6)$$

Starting from this equation, we can carry out an analysis very similar to the one in chapter 6 for a simple compressible substance. The only difference is that we replace -v by m, and P by H. For example, we can define a magnetic enthalpy, Helmholtz free energy, and Gibbs free energy by

$$h = u - Hm \tag{12.7}$$

$$f = u - Ts \tag{12.8}$$

$$g = h - Ts = u - Ts - Hm.$$
 (12.9)

Although we use the same symbols for these as we did for a simple compressible substance, it's important to keep in mind the difference in definition (e.g. h = u - Hm, not h = u + Pv) since the reversible work mode is now magnetization, not compression.

The differential equations of state for these properties are:

$$dh = Tds - mdH \tag{12.10}$$

$$df = -sdT + Hdm \tag{12.11}$$

$$dg = -sdT - mdH (12.12)$$

Integratings these equations would yield u(s, m), h(s, H), f(T, m), and g(T, H), all of which are fundamental relations. Experimentally, it is usually easiest to work with temperature and magnetic field strength as independent variables, so g(T, H) is in many cases the most useful of these fundamental relations.

Of course, analogs of the Maxwell relations may be easily written down.

The above differential equations of state are general and apply to any simple magnetic substance. To determine the specific properties of a particular substance, we need to know the functional form of one of the fundamental relations [say, g(T, H)] or else a set of experimental equations of state like m(T, H) and $c_H(T, H)$. Let's look at a couple of important magnetic substances.

12.2.1 The Curie Substance

For paramagnetic materials, the tendency for the dipoles to be aligned with the field is balanced by the effects of random collisions (in a gas) or vibrations of the lattice (in a solid), which tend to randomize the direction the dipole points. Since the energy associated with the random, thermal motion scales with temperature, we expect that the magnetization of a paramagnetic material will increase with H at constant T, and decrease with T at constant H. In fact it is found that M = f(H/T). The function f(H/T) is linear for small H/T, and saturates at an asymptotic value for large H/T, since in this limit the dipoles are perfectly aligned and therefore M can't increase further.

A Curie substance is defined as any substance which obeys

$$\vec{M} = C\frac{\vec{H}}{T}.$$
(12.13)

All paramagnetic substances have this behavior for small H/T. In terms of m, or

$$m = C' \frac{\vec{H}}{T},\tag{12.14}$$

where $C' = \mu_0 v C$.

Like an ideal gas, a Curie substance has an internal energy which depends only on temperature. The proof follows exactly the procedure we used to prove u = u(T) for an ideal gas. First solve Eq. (12.6) for ds:

$$ds = \frac{1}{T}du - \frac{H}{T}dm.$$
(12.15)

Substituting for H/M,

$$ds = \frac{1}{T}du - \frac{1}{C'}mdm.$$
 (12.16)

Equating mixed partial derivatives,

$$\frac{\partial}{\partial m} \left[\frac{1}{T} \right]_{u} = -\frac{1}{C'} \left(\frac{\partial m}{\partial u} \right)_{m} \tag{12.17}$$

But $(\partial m/\partial u)_m = 0$, so 1/T depends only on u, not on m. Therefore, T = T(u), and inverting this we have u = u(T).

In fact, it can be seen from this analysis that any material which obeys

$$m = f(H/T) \tag{12.18}$$

will have an internal energy which is a function of temperature alone.

Knowing that u = u(T), we may now integrate the Gibbs equation and find the entropy of a Curie substance.

$$ds = \left(\frac{1}{T}\right) \left(\frac{du}{dT}\right) dT - \frac{H}{T} dm.$$
(12.19)

The coefficient multiplying dT is $(\partial s/\partial T)_m$, which by definition is c_m/T , where c_m is the specific heat at constant magnetization. Therefore, we see

$$c_m(T) = \frac{du(T)}{dT} \tag{12.20}$$

which is a function only of temperature for a Curie substance. The Gibbs equation then is

$$ds = \frac{c_m(T)}{T}dT - \frac{H}{T}dm.$$
(12.21)

Since m = C'H/T,

$$ds = \frac{c_m(T)}{T}dT - \frac{m}{C'}dm.$$
(12.22)

Integrating this,

$$s(T_1, m_1) - s(T_0, m_0) = \int_{T_0}^{T_1} \frac{c_m(T)}{T} dT - \frac{1}{2C'} \left(m_1^2 - m_0^2 \right), \qquad (12.23)$$

or in terms of M,

$$s(T_1, M_1) - s(T_0, M_0) = \int_{T_0}^{T_1} \frac{c_m(T)}{T} dT - \frac{\mu_0 v}{2C} \left(M_1^2 - M_0^2 \right), \qquad (12.24)$$

Note that the entropy decreases if a Curie substance is magnetized isothermally. This makes sense physically: as individual atomic magnetic dipoles become more aligned with the field (increasing M), the sample becomes more ordered. Therefore, we would expect s to decrease, as it does.

This also means that heat must be removed from the sample during isothermal magnetization. If a sample is magnetized reversibly at T from zero magnetization to some value M,

$$Q = \frac{\mu_0 v M^2}{2C}$$
(12.25)

must be rejected to the environment. If instead the sample is magnetized adiabatically, then it will increase in temperature. Similarly, if a Curie substance is demagnetized (M decreased) at constant temperature, heat must be supplied. If demagnetization is carried out adiabatically, the temperature will decrease.

Thus, magnetizing a Curie substance is similar to compressing a gas, and demagnetizing a Curie substance is similar to expanding a gas. This analogy suggests it should be possible to construct a heat pump or a heat engine by taking a Curie substance through a sequence of states in the (T, m) plane (or equivalently, the (T, H) plane) returning to the initial state. While no known practical heat engine operates on this cycle, it is in fact used as a heat pump (refrigerator) to reach very low temperatures near absolute zero. Temperatures as low as 10^{-8} K have been reached using magnetic refrigerators. To reach these very low temperatures, nuclear magnetic moments (rather than atomic ones) are employed.

12.3 Superconductors

Many metals exhibit superconductivity when cooled to very low temperatures. This effect was first discovered by Onnes in 1911, shortly after he succeeded in liquifying helium. Until 1986, all known superconductors required cooling below 20 K before they would become superconductors. Beginning in 1986, some ceramic materials which become superconductors at abnormally high temperatures (above 100 K) were discovered. One of the most useful ones is yttrium barium copper oxide: $YBa_2Cu_3O_{7-x}$. The discovery of high temperature superconductors has enormous practical consequences, since their transition temperatures are above the boiling point of N₂ at 1 atm. Therefore, inexpensive liquid nitrogen can be used to keep these materials superconducting, rather than expensive liquid helium which is required for most lower-temperature superconductors.

Superconductors exhibit several strange properties. As they are cooled below

the transition temperature T_c , the electrical resistance drops suddenly to exactly zero. If a current is set up in a superconducting ring (for example by cooling it below T_c in a magnetic field and then removing the field), it persists indefinitely. Measurements have been done which show currents remaining unchanged for months. This can only be possible if the resistance is really zero, not just very small.

If a superconductor is brought into a magnetic field, currents will flow in the surface layer of the superconductor, which perfectly shield the the magnetic field from the interior, so that the magnetic field inside is zero. This is the behavior predicted from EM theory for any perfect conductor. In contrast, for a real conductor with finite resistance, the induced currents would eventually die out and the field would penetrate.

But superconductors display an additional property which is not simply a consequence of zero resistance. If a superconducting material is cooled from above T_c to below T_c in a magnetic field, the magnetic field is completely expelled from the interior at T_c . Since the magnetic field penetrates above T_c , there would be no reason for currents to start flowing in the surface to shield the interior from the magnetic field, if a superconductor were just like a metal with zero resistance.

But the currents do start flowing in the surface layer at T_c , and the field is expelled. Evidently, there is something intrinsic about the superconducting state which is incompatible with the presence of a magnetic field inside. This effect, first discovered in 1933 by Meissner and Ochsenfeld, is called the *Meissner effect*. This is what causes a permanent magnet to levitate above a superconducting dish, and is employed in several schemes for magnetic levitation trains.

Thermodynamics can be used to understand some of the properties of superconductors. When a superconductor expels a magnetic field it does magnetic work on the external currents producing the field, so magnetic work is a relevant work mode for a superconductor. In principle, we could include -Pdv work too, but it is usually acceptable to assume the superconductor is incompressible. In this case, a superconductor is a simple magnetic substance.

It is found that applying a sufficiently strong magnetic field to a superconductor can destroy the superconductivity, causing it to revert to the "normal" state. We may regard the superconducting state exactly like a thermodynamic phase. The phase diagram for a superconductor looks something like shown below.



What is the magnetic equation of state of a superconductor? Since we know $\vec{B} = 0$ in a superconductor, and also

$$\vec{B} = \mu_0 (\vec{H} + \vec{M})$$
 (12.26)

the magnetic equation of state in the superconducting state is

$$\vec{M} = -\vec{H}.\tag{12.27}$$

In contrast, in the normal state, $\vec{M} = 0$ since typically metals which become superconducting do not contain paramagnetic ions.

Since the Gibbs free energy is particularly useful if T and H are held constant, let's calculate g for the normal and superconducting phases. We can do this by integrating the differential equation of state

$$dg = -sdT - mdH, (12.28)$$

using the appropriate magnetic equation of state for the normal and superconducting phases $(m = 0 \text{ or } m = -\mu_0 v H)$.

For the normal phase, m = 0, and therefore Hdm = 0 so it is impossible to do magnetic work on the substance when it is in the normal phase. As in the case of an incompressible fluid, this means that the properties of the substance in the normal state are fixed by only one quantity, the temperature. For the free energy we have

$$dg_n = -s_n(T)dT. (12.29)$$

Therefore,

$$g_n(T_1) - g_n(T_0) = -\int_{T_0}^{T_1} s_n(T) \, dT.$$
(12.30)

For the superconducting phase,

$$dg_s = -s_s dT - m_s dH = -s_s dT + (\mu_0 v H) dH.$$
(12.31)

If we equate the mixed partial derivatives of the coefficients in this equation,

$$-\left(\frac{\partial s_s}{\partial H}\right)_T = \mu_0 v \left(\frac{\partial H}{\partial T}\right)_H = 0, \qquad (12.32)$$

we see that the entropy in the superconducting phase has no dependence on H, and therefore depends only on T. Thus, s is a function just of T for both the superconducting and normal phases. (Note that this was not true for the Curie substance.)

With this information, we can proceed to integrate Eq. (12.31) to find the Gibbs free energy of a superconductor.

$$g_s(T_1, H_1) - g_s(T_0, H_0) = -\int_{T_0}^{T_1} s_s(T) \, dT + \frac{\mu_0 v}{2} \left(H_1^2 - H_0^2\right).$$
(12.33)

We showed in Chapter six that the stable phase of a simple compressible substance at specified (T, P) is the one with the lowest Gibbs free energy g = u + Pv - Ts. The same analysis can be repeated for the magnetic case, simply replacing P with H and v with -m to show that the stable phase of a simple magnetic substance at specified (T, H) is the one with lowest magnetic Gibbs free energy g = u - Hm - Ts.

Therefore, in the region of the (H, T) plane where the superconducting phase is thermodynamically stable, $g_s < g_n$; outside this region $g_n < g_s$. On the coexistence line where they can exist in equilibrium with one another $g_s = g_n$.

Let's consider a temperature $T < T_c$, where the superconducting phase is stable for H = 0, and so $g_s(T,0) < g_n(T)$. Consider what happens as the magnetic field is increased from zero. The Gibbs free energy of the normal phase (metastable at H = 0) is not affected by H. But the Gibbs free energy of the superconducting phase increases quadratically with H. As shown in Figure 12.1, $g_s(T, H)$ becomes equal to $g_n(T)$ at some value of H; this defines the value of the critical magnetic field strength $H_c(T)$, above which the superconductor reverts to the normal phase:

$$g_s(T, H_c) = g_n(T)$$

$$g_s(T, 0) + \frac{\mu_0 v H_c^2}{2} = g_n(T).$$
(12.34)

(12.35)

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Figure 12.1: Gibbs free energy for the superconducting and normal phases.

Therefore,

$$H_c^2(T) = \frac{2}{\mu_0 v} \left(g_n(T) - g_s(T, 0) \right).$$
(12.36)

Note that the work done by the superconductor on the surroundings to keep the magnetic field out as the external field is raised from zero to H is

$$W = -\int_{0}^{H} H dm = +\mu_{0} v \int_{0}^{H} H dH = \frac{\mu_{0} v}{2} H^{2}.$$
 (12.37)

So the increase in Gibbs free energy of the superconductor is due to the work it has to do to keep the field out; eventually, (at H_c) it is no longer worth it energetically and the substance reverts to the normal phase and lets the field in.

Now consider the latent heat associated with the normal to superconducting transition. Doing entropy accounting for a substance which undergoes a phase change from the normal to the superconducting state,

$$s_s(T) = s_n(T) + \frac{Q}{T},$$
 (12.38)

where Q is the heat added to bring about the normal \rightarrow superconducting transition.

Since $s = -(\partial g/\partial T)_H$,

$$\begin{aligned} Q &= T\left(s_s(T) - s_n(T)\right) \\ &= -T\left(\frac{\partial(g_s(T, H) - g_n(T))}{\partial T}\right) \\ &= -T\left(\frac{\partial(g_s(T, 0) + \mu_0 v H^2 - g_n(T))}{\partial T}\right) \\ &= -T\left(\frac{d(g_s(T, 0) - g_n(T))}{dT}\right) \end{aligned}$$

$$= T\left(\frac{d(\mu_0 v H_c^2(T)/2)}{dT}\right)$$
(12.39)

(12.40)

Therefore,

$$Q = \mu_0 v T H_c(T) \frac{dH_c(T)}{dT}$$
(12.41)

From the phase diagram, we see that $H_c = 0$ at T_c , and the transition occurs at $T < T_c$ if a field is applied. Therefore, from Eq. (12.41), at zero applied field the normal \rightarrow superconducting transition has a latent heat of zero. Also, as $T \rightarrow 0, Q \rightarrow 0$, so |Q| must have a maximum at a temperature between 0 and T_c . Since $dH_c(T)/dT < 0, Q < 0$ for non-zero H. Thus, when a substance is cooled and becomes superconducting, heat is given off, similar to when a gas condenses to form a liquid.

Finally, we can derive an expression for the difference between the specific heats of the normal and superconducting phases. Since for both phases the entropy is a function only of temperature, the specific heat is simply c = T(ds/dT), and is the same whether H or m is held constant.

Since $s_s(T) - s_n(T) = Q/T$, we have from Eq. (12.41)

$$s_s(T) - s_n(T) = \mu_0 v H_c(T) \frac{dH_c(T)}{dT}$$
 (12.42)

Differentiating with respect to T and multiplying by T,

$$c_s(T) - c_n(T) = \mu_0 v T \left[\left(\frac{dH_c(T)}{dT} \right)^2 + H_c(T) \frac{d^2 H_c}{dT^2} \right].$$
 (12.43)

At zero field, the transition occurs at $T = T_c$. Since $H_c = 0$ in this case,

$$c_s(T_c) - c_n(T_c) = \mu_0 v T_c \left(\frac{dH_c(T)}{dT}\right)_{T=T_c}^2.$$
 (12.44)

This important formula, known as *Rutger's formula*, shows that there will be a jump in specific heat as the substance is cooled below T_c and becomes superconducting. The magnitude of the jump depends only on v, T_c , and the slope of the coexistence curve at $T = T_c$. The specific heat of tin is shown in Figure 12.2, which illustrates the jump in specific heat when the tin becomes superconducting.

This relationship provides a good way to determine how much of a sample is superconducting. In many cases, a sample may have impurities or other phases

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Figure 12.2: The specific heat of tin as a function of temperature. Open circles: no magnetic field; solid circles: $H > H_c$ (normal phase); dotted line: electron contribution to normal specific heat; dashed line: lattice contribution to normal specific heat. From W. Buckel, *Superconductivity: Fundamentals and Applications*, VCH, 1991.

present which do not become superconducting. As long as the superconducting portion forms a continuous network, the electrical resistance will be zero, even if the superconduction portion is very small. But the jump in specific heat is dependent on the amount of the sample which undergoes the phase transition (through v) and so can be used to determine the superconducting fraction.

12.3.1 Microscopic Interpretation

The results derived above were based on a few experimental observations, such as the Meissner effect (M = -H). They did not require us to know anything about what causes superconductivity, or why M = -H. In fact, these thermodynamic results were known long before a satisfactory microscopic theory of superconductivity had been developed.

The theory which finally gave a clear microscopic picture of superconductivity was developed in the 1950's by Bardeen, Cooper, and Schrieffer, and their theory is known as the BCS theory. The BCS theory shows that the reason some materials become superconducting at low temperature is that the electrons pair up in quantum-mechanical bound states called "Cooper pairs." The pairing is brought about by an interaction between the electrons and the positivey-charged lattice. Since an electron has negative charge, the lattice atoms near an electron are attracted to it, leading to excess positive charge around an electron. This positive charge in turn attracts another electrons, which creates an "effective" attractive interaction between the two electrons. Of course, the electrons also repel one another, but in some cases the attractive interaction can be stronger than the repulsion and the two electrons become bound together.

The situation is actually very similar to how two protons and two electrons bind together to form an H_2 molecule. Even though the electrons repel one another and so do the protons, by keeping the electrons most of the time between the protons, the electron-proton attraction is greater than the proton-proton and electron-electron repulsion and a stable molecule forms. The electrons and postively-charged lattice distortions ("phonons") arrange themselves similarly to form a stable Cooper pair. Just like a molecule, a Cooper pair requires energy to break it up.

It turns out that the number of Cooper pairs $n_c(T)$ is a function of temperature, but hardly depends on H. The number of pairs goes continuously to zero at $T = T_c$. This is why the specific heat of a superconductor is greater than in the normal phase – it requires energy to break up some Cooper pairs if the temperature is raised.

A Cooper pair has zero total angular momentum, and so are bosons obeying

Bose-Einstein statistics (the individual electrons, in contrast are fermions and obey Fermi-Dirac statistics). There is no restriction on the number of bosons which can occupy a single quantum level. In fact, the BCS theory shows the most-stable state of the system (the ground state) is one in which *all* Cooper pairs occupy the *same* quantum state. Thus, a single quantum-mechanical wavefunction which extends throughout the superconductor describes all of the Cooper pairs, which are rigidly locked together in phase (much like photons in laser light). It is this macroscopic quantum-mechanical aspect which is responsible for all of the strange properties such as zero resistance.