The Form of Magnetic Work in a Fundamental Thermodynamic Equation for a Paramagnet

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Abstract

Magnetic work takes two forms in the thermodynamics of a paramagnet as developed in many textbooks. We observe that in the case when the lattice energy is excluded, the form $\delta W = BdM$ cannot be used in a fundamental thermodynamic equation. This shows that there are thermodynamic systems with no fundamental thermodynamic equation.

The thermal physics of magnetic systems has been the source of continuing confusion. Mandl writes in the second edition of his text,[1] "As is well known, the thermodynamic discussion of magnetic systems easily leads to misleading or even wrong statements, and I fear that the first edition was not free from these." And according to Kittel,[2] "A great deal of unnecessary confusion exists as to how to write the First Law of Thermodynamics for a magnetic system."

For a paramagnetic crystal in a uniform magnetic field B, with total magnetic dipole moment M, there are two forms for the work done when B and M change:

$$\delta W_{ms} = BdM \text{ and } \delta W_s = -MdB. \tag{1}$$

The form δW_{ms} applies when the mutual field energy is included in the system, the form δW_s when it is not.[3] The forms δW_{ms} and δW_s are readily derived also by means of statistical mechanics; we include these derivations in the appendix.

The thermodynamic derivations of these forms given by Mandl,[4] Kittel,[5]

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[1] F. Mandl, Statistical Physics (Wiley, Chichester, 1988), 2nd ed., p. vii.

[2] Charles Kittel, Elementary Statistical Physics (Wiley, New York, 1958), pp. 77-82.

[3] We take the paramagnetic spin system to be *ideal*: interaction among the dipole spins is essentially absent. The model which results from this assumption is widely used, is an excellent approximation to real systems within its domain of application, and does not obey the third law of thermodynamics. It shares all these attributes with the ideal gas model.

[4] Reference 1, pp. 21-28 and 336-339.

[5] Reference 2, pp. 77-82.

and Callen[6] make no explicit reference to the crystal lattice. They assume that the volume of the crystal does not change when a change in the magnetic field is imposed; with this assumption, no work is done on the lattice alone. Consequently, the work forms are valid whether or not the lattice is included in the system. The form $\delta W_s = -MdB$ thus applies to the systems $\mathcal{P}_s$ (whose internal energy is just the potential energy of the spins in the field) and $\mathcal{P}_{sl}$ (which includes the lattice energy as well). The form $\delta W_{ms} = BdM$ applies to the systems $\mathcal{P}_{ms}$ and $\mathcal{P}_{msl}$, which add the mutual field energy to the first two systems.

Now $\mathcal{P}_s$ and $\mathcal{P}_{ms}$, to which the lattice is external, are bona fide thermodynamic systems, exchanging heat and work with their environment, possessing an internal energy, entropy, and temperature, and obeying the first and second laws of thermodynamics. The systems are in no way "unphysical" or "unrealistic." Indeed, the thermal physics of $\mathcal{P}_s$ has well-known applications. For example, adiabatic cooling is explained in some elementary texts by consideration just of $\mathcal{P}_s$, with only passing reference to the lattice.[7] And the statistical mechanics of $\mathcal{P}_s$ takes a particularly simple form, so it appears frequently in developments of elementary concepts.[8]

Notice that we do not assume that the spins are adiabatically separated from the lattice, only that any heat transfer to the lattice is considered a transfer of energy out of the system. Notwithstanding, the relaxation time between nuclear spins and the lattice is so slow that these spin systems may be considered isolated from the lattice.[9] The realization that such spin systems are thermodynamic systems in their own right underlies the modern recognition of the existence of negative absolute temperatures.

Both δW_{ms} and δW_s lead to correct forms of the first law:

$$dU = \delta Q + BdM \tag{2}$$

applies to the systems $\mathcal{P}_{ms}$ and $\mathcal{P}_{msl}$, while

$$dU = \delta Q - MdB \tag{3}$$

applies to $\mathcal{P}_s$ and $\mathcal{P}_{sl}$.

Since $\delta Q = TdS$ for reversible changes, we have, *algebraically,*

$$dU = TdS + BdM \tag{4}$$

for $\mathcal{P}_{ms}$ and $\mathcal{P}_{msl}$, and

$$dU = TdS - MdB \tag{5}$$

[6]Herbert Callen, Thermodynamics and an Introduction to Thermostatics, (Wiley, New York, 1985), 2nd ed., pp. 479-485.

[7]Reference 1, pp. 139-145; Tony Guenalt, Statistical Physics, (Routledge, London and New York, 1988), pp. 38-43.

[8]Charles Kittel and Herbert Kroemer, Thermal Physics (Freeman, San Francisco, 1980), 2nd ed., pp. 62-64, 69-70.

[9]M. Toda, R. Kubo, and N. Saitô, Statistical Physics I (Springer-Verlag, Berlin, 1995), 2nd ed., p. 67.

for $\mathcal{P}_s$ and $\mathcal{P}_{sl}$.

It might appear that we have obtained fundamental thermodynamic equations (FTEs) for our four systems. A *fundamental thermodynamic equation* (or *relation*) is an equation

$$dU = TdS + YdX, \qquad (6)$$

expressing the total differential of the energy function of the system in terms of S and other independent variable(s) X.[10]

Eq. (5) is a valid FTE for $\mathcal{P}_s$ and $\mathcal{P}_{sl}$, the systems in which the mutual field energy is excluded. And Eq. (4) is a valid FTE for $\mathcal{P}_{msl}$. But we shall show that Eq. (4) *cannot* be regarded as an FTE for $\mathcal{P}_{ms}$. This system has peculiarities which seem not to have been noted before. They are worthy of attention for several reasons. Since the aforementioned authors do not even mention the lattice in their derivations of δW_{ms}, it is easy to fall into the belief that Eq. (4) is a valid FTE for $\mathcal{P}_{ms}$, just as Eq. (5) is valid for $\mathcal{P}_s$. No author points out that Eq. (4) is an FTE only if the lattice energy is included. The example of $\mathcal{P}_{ms}$ shows that one cannot simply and automatically replace δQ with TdS in the expression of the first law and obtain an FTE. We see below, in fact, that $\mathcal{P}_{ms}$ furnishes an example of a thermodynamic system which has no FTE.

An FTE (Eq. (6)) is more than just an algebraic relationship among its constituent quantities. (A) Since it exhibits a total differential, S and X are independent, and the coefficients T and Y are partial derivatives of U. (B) Physically, S and X suffice to completely determine the state of the thermodynamic system.[11] Moreover, the energy function $U(S, X)$ contains all thermodynamic information about the system.[12]

Much of the thermodynamic formalism is built on these requirements. Yet Eq. (4) applied to $\mathcal{P}_{ms}$ fails them both, as we now describe.

(A) requires that S and M be independent variables. But in $\mathcal{P}_{ms}$ (and in $\mathcal{P}_s$), $S = S_{ms} = S_s$ is a function of M alone: $S = S(M)$. For S is a function of the probability $p = p$(spin up): $S = Nk_B(-p\ln p - (1-p)\ln(1-p))$. p in turn is a function of the quantity $x = mB/kT$: $p = e^x/(e^x + e^{-x})$; the denominator is the partition function for a 1-particle system. Finally, x is a function of M by the equation of state $M = Nm \tanh x$. (The explicit formula for S in terms of M is derived in the appendix.)

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[10]Our terminology is in agreement with common usage; see for example reference 1, p. 86 and David Chandler, Introduction to Modern Statistical Mechanics, (Oxford University Press, New York, 1987), p. 10. The energy might be expressed as a function of different independent variables, so we do not assume that an FTE for a system is unique. However, we do not use the term FTE to refer to equations expressing differentials of Legendre transforms of the energy (or of the entropy).

[11]As is customary when dealing with paramagnetic solids, we take N and V to be constant; therefore, they need not appear in a fundamental equation.

[12]Reference 6, pp. 28-29. Callen says that "once the fundamental relation of a system is known, every thermodynamic attribute is completely and precisely determined." He means by *fundamental relation* the expression of the energy (or the entropy), not the differential of the energy, as a function of its independent variables. The difference in terminology makes no difference for (B): since U is defined only up to an additive constant, U and dU can each be recovered from the other and contain the same information.

(The entropy S_{msl} is not a function of M, so that Eq. (4) *is* a valid fundamental thermodynamic equation for $\mathcal{P}_{msl}$. Proof: S_{msl} is the sum of the spin entropy, which by the preceding paragraph is a function of M, and the lattice entropy, which is an increasing function of T. If S_{msl} were a function of M, i.e., $S_s(M) + S_l(T) = f(M)$, a change in T would necessarily change M. But this is not the case: by the equation of state, M is a function of B/T, and so the change in T can be followed by an isothermal change in B to restore M to its original value.)

The spins in our paramagnetic crystal have total potential energy $U_s = -MB$ in the magnetic field, while the mutual field energy is MB.[13] Thus the energy of the system $\mathcal{P}_{ms}$ is

$$U_{ms} = U_s + U_m = -MB + MB \equiv 0! \qquad (7)$$

All partial derivatives of U_{ms} are therefore identically 0 over the state space; but the coefficients in Eq. (4) are not.

As for (B), S and M do not by themselves determine the thermodynamic state of $\mathcal{P}_{ms}$. Specifying S and M determines p and thereby x. x determines the ratio B/T, but there are infinitely many values of B and T which yield this ratio; each such pair of values corresponds to a different state of the system consistent with the given S and M.

Since Eq. (4) fails (A) and (B), it cannot be an FTE for $\mathcal{P}_{ms}$. In fact, since $U_{ms} \equiv 0$ clearly does not contain all thermodynamic information about this system, *there is no FTE for $\mathcal{P}_{ms}$*.

If one *does* take Eq. (4) (or any equation) to be an FTE for $\mathcal{P}_{ms}$, then the thermodynamic formalism produces incorrect results, two of which we now describe.

The temperature of $\mathcal{P}_{ms}$ may be obtained by setting $U_{ms} = 0$ in (the algebraically correct) Eq. (4) and solving for T: $T = -M'(S_{ms})B$; or it may be obtained from the appendix since it is the same as the temperature of $\mathcal{P}_s$. If $\mathcal{P}_{ms}$ possessed an FTE (Eq. (6)), then the thermodynamic formalism would *define* $T = (\partial U_{ms}/\partial S_{ms})_X \equiv 0$, which is not correct. In Eq. (4) for $\mathcal{P}_{ms}$, $S = S_{ms}$ and M are not independent (as discussed under (A)), and so the partial $(\partial U_{ms}/\partial S)_M$ does not even exist, since one cannot vary S while keeping M fixed.

Maxwell's relations express the equality of the second order mixed partials of U. If Eq. (4) were an FTE for $\mathcal{P}_{ms}$, then we could read off the Maxwell relation $(\partial T/\partial M)_S = (\partial B/\partial S)_M$. As in the previous paragraph, this has no meaning for $\mathcal{P}_{ms}$ since one cannot hold one of S and M fixed while varying the other. Eq. (5) gives $(\partial T/\partial B)_S = -(\partial M/\partial S)_B$ for $\mathcal{P}_s$. Since all quantities in this expression have the same value for $\mathcal{P}_s$ and $\mathcal{P}_{ms}$, the expression is also valid for $\mathcal{P}_{ms}$.

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[13]Reference 1, p. 26.

In spite of the foregoing considerations, one might argue as follows. From Eq. (5) for $\mathcal{P}_s$, $U_s = U_s(S_s, B)$. Take the Legendre transform with respect to B to obtain the "enthalpy" $H(S_s, M) = U_s + MB$. Then $dH = TdS_s + BdM$. Since $S_{ms} = S_s$, the right side is the same as the right side of Eq. (4) for $\mathcal{P}_{ms}$, which therefore *is* a total differential, contradicting our earlier claims. But $U_s = -MB$ and so $H \equiv 0$. Thus H can no more serve as a thermodynamic potential for $\mathcal{P}_{ms}$ than can U_{ms}. (Cf. Eq. 7 et seq.)

Appendix: Statistical Mechanics of the System $\mathcal{P}_s$.

Here we collect for reference the derivation of the properties of the N-particle paramagnetic spin system $\mathcal{P}_s$ discussed in the article. The canonical ensemble is understood in what follows.

We label the two eigenstates of a single-particle system "spin-up" and "spin-down", with potential energies in the uniform field $\varepsilon_1 = -mB$ and $\varepsilon_2 = +mB$. Let $x = mB/k_B T$. Then the single-particle partition function is $Z_1 = e^x + e^{-x}$ and the probabilities of the eigenstates are $p = \Pr(\varepsilon_1) = e^x/Z_1$; $q = \Pr(\varepsilon_2) = 1 - p = e^{-x}/Z_1$. As an immediate consequence,

$$\ln p - \ln q = 2x = 2mB/k_B T \tag{8}$$

The (mean) total magnetic moment is $M = Nm(p - q) = Nm(2p - 1) = NM_1$, where M_1 denotes the mean total magnetic moment per particle. Inserting $p = e^x/Z_1$ into this expression gives the *equation of state* for paramagnetic systems:

$$M = Nm \tanh x. \tag{9}$$

In particular we see that M is a function of B/T. Rearranging the first expression for M gives $p = 1/2 + M/2mN$ and $q = 1/2 - M/2mN$. If we substitute these values for p and q in (8), we get

$$T = \frac{mB}{k_B[\ln(m - M/N) - \ln(m + M/N)]}.$$

The entropy is defined as $S = NS_1 = Nk_B[-p \ln p - q \ln q]$, where S_1 is the entropy per particle. Substituting for p and q, S can be written as a function of M as asserted in the article:

$$S = Nk_B \left[-\left(\frac{1}{2} + \frac{M}{2mN} \right) \ln \left(\frac{1}{2} + \frac{M}{2mN} \right) - \left(\frac{1}{2} - \frac{M}{2mN} \right) \ln \left(\frac{1}{2} - \frac{M}{2mN} \right) \right]$$

Next we compute dS_1, using Eq. (8), and dM_1:

$$\begin{aligned} dS_1 &= -k_B d[p \ln p + q \ln q] = -k_B[dp(1 + \ln p) - dp(1 + \ln q)] \\ &= k_B[dp(\ln p - \ln q)] = \frac{-2mB}{T} dp \\ dM_1 &= d(m(2p - 1)) = 2m\,dp \end{aligned}$$

Therefore,

$$TdS = TNdS_1 = TN\frac{-B}{T}dM_1 = -BdM. \tag{10}$$

The mean energy per particle is the expected value of the eigenenergies, $\varepsilon_1 p + \varepsilon_2 q = -mB(p-q)$. The (mean) energy of the whole system is $U_s = N(-mB(p-q)) = -MB$. The differential of U_s is

$$dU_s = -BdM - MdB = TdS - MdB, \tag{11}$$

thus establishing an FTE for $\mathcal{P}_s$. Eq. (11) and Eq. (10) together show that for reversible changes (i.e., $\delta Q = TdS$) in a system with fixed N, the work is $\delta W_s = -MdB$.

For the system $\mathcal{P}_{ms}$, which includes the mutual field energy, the internal energy is 0, but the temperature and the entropy are the same as in $\mathcal{P}_s$. For reversible changes, we have by Eq. (10)

$$0 = dU_{ms} = \delta Q_{ms} + \delta W_{ms} = TdS + \delta W_{ms} = -BdM + \delta W_{ms},$$

and so the work is $\delta W_{ms} = BdM$.

As a final application of the statistical mechanics, we offer a short derivation of Eq. (5) and Eq. (4) for the systems $\mathcal{P}_{sl}$ and $\mathcal{P}_{msl}$, respectively. We write $U_m = MB$ for the mutual field energy, $U_s = -MB$ for the spin potential energy, and U_l for the lattice energy; we write S_s instead of S for the spin entropy to keep it distinct from S_l, the lattice entropy. Taking differentials,

$$\begin{aligned} dU_m = &\ d(MB) = BdM + MdB \\ dU_s = &\ d(-MB) = -BdM - MdB = TdS_s - MdB \\ dU_l = &\ TdS_l \end{aligned} \tag{12}$$

The second line uses Eq. (10). The third line contains no work term because the volume is essentially constant. We may use the same T in both the second and third lines because the spins and the lattice are thermally coupled and assumed to be in equilibrium.

Adding the second and third lines of Eqs. (12) gives

$$dU_{sl} = d(U_s + U_l) = Td(S_s + S_l) - MdB = TdS_{sl} - MdB. \tag{13}$$

Adding all three lines gives

$$dU_{msl} = d(U_m + U_s + U_l) = Td(S_s + S_l) + BdM = TdS_{msl} + BdM. \tag{14}$$