Free energies in the presence of electric and magnetic fields

Onuttom Narayan and A. P. Young

Department of Physics, University of California, Santa Cruz, California 95064

We discuss different free energies for materials in static electric and magnetic fields. We explain what the corresponding Hamiltonians are, and describe which choice gives rise to which result for the free energy change, \( dF \), in the thermodynamic identity. We also discuss which Hamiltonian is the most appropriate for calculations using statistical mechanics, as well as the relationship between the various free energies and the “Landau function”, which has to be minimized to determine the equilibrium polarization or magnetization, and is central to Landau’s theory of second order phase transitions.

I. INTRODUCTION

One frequently needs to calculate the properties of materials in magnetic or electric fields using statistical mechanics. The procedure, of course, is to start from “the Hamiltonian”, perform the statistical sum to get the partition function, the logarithm of which gives “the free energy”. Unfortunately, there is much confusion in the literature because different authors include different pieces of the energy of the electric or magnetic field in the Hamiltonian, generally without explaining precisely what they are doing. In this paper we describe the different results that are given for the cases of static electric fields and static magnetic fields, show the relations between them, and explain which choice gives rise to which result for the free energy change \( dF \) in the thermodynamic identity. We also discuss which Hamiltonian, and hence free energy, is the most appropriate. Finally we describe the connection between the various free energies and the “Landau function” which has to be minimized in Landau’s theory of second order phase transitions.

We use rationalized Gaussian units throughout, since this encumbers the formulae with a minimum number of factors for units and numerical factors. We also set \( \hbar = c = 1 \).

II. LAGRANGIAN AND HAMILTONIAN

For a charged particle in an electromagnetic field the Lagrangian is

\[
L = \frac{1}{2}m\dot{x}_0^2 + q\dot{x}_0 \cdot A(x_0) - q\phi(x_0) + \frac{1}{2} \int dx \left[ E^2 - B^2 \right],
\]

where \( x_0 \) and \( \dot{x}_0 \) are the position and velocity of the particle which has charge \( q \), and the scalar potential \( \phi \) and vector potential \( A \) are related to the electric and magnetic fields by \( E = -\nabla \phi - \partial_t A \) and \( B = \nabla \times A \). This parametrization automatically ensures that \( \nabla \times E = 0 \) and \( \nabla \cdot B = 0 \). The justification for this Lagrangian is that the Euler-Lagrange equations of motion derived from it for \( \phi, A \) and \( x_0 \) correctly give the remaining two (inhomogeneous) Maxwell’s equations, with charge density and current density given by

\[
\rho(x) = q\delta(x - x_0), \quad J(x) = q\dot{x}_0 \delta(x - x_0),
\]

as well as the equation of motion for the particle under the Lorentz force.

For statistical mechanics we need the Hamiltonian, and to obtain this from the Lagrangian in Eq. (1), we first have to construct the canonical momenta. There is no canonical momentum for \( \phi \) since \( L \) does not depend on \( \partial_t \phi \); \( \phi \) is not a dynamical variable. For the other degrees of freedom, we have \( p_0 \equiv \partial L/\partial \dot{x}_0 = m\dot{x}_0 + qA \) and \( \Pi_A \equiv \partial L/\partial \partial_t A = \nabla \phi + \partial_t A = -E \). Hence the Hamiltonian is equal to

\[
\mathcal{H} = p_0 \cdot \dot{x}_0 + \int dx \left( \Pi_A \cdot \partial_t A \right) - L
\]

\[
= \frac{1}{2m} \left( p_0 - qA(x_0) \right)^2 + q\phi(x_0)
\]

\[
+ \int dx \left\{ \frac{1}{2} \left[ (\nabla \times A)^2 + \Pi_A^2 \right] - \nabla \phi \cdot \Pi_A \right\}
\]

Applying Hamilton’s equations of motion to Eq. (3) gives Maxwell’s equations and the equation of motion for the particle under the Lorentz force, as required. Equation (3) can be simplified by noting that since \( \phi \) is not a dynamical variable, we can insert the condition

\[
\nabla \cdot E = \rho \tag{4}
\]

corresponding to \( \partial_\phi L = -\partial_\phi \mathcal{H} = 0 \), in the Hamiltonian itself. Since \( \Pi_A = -E \), the last term in Eq. (3) can be rearranged as

\[
\int dx \nabla \phi \cdot E = - \int dx \phi \nabla \cdot E = - \int dx \delta \phi = -q\phi(x_0),
\]

in which we integrated by parts in the first step, used Eq. (1) in the second step, and used Eq. (2) in the last step. Hence this term cancels the \( +q\phi(x_0) \) term in the Hamiltonian, Eq. (3). The Hamiltonian can therefore...
be simplified to

\[ \mathcal{H} = \frac{1}{2m} \left( p_0 - qA(x_0) \right)^2 - \gamma s \cdot B + \frac{1}{2} \int d\mathbf{x} \left[ \mathbf{E}^2 + \mathbf{B}^2 \right], \]

in which the condition \( \nabla \cdot \mathbf{E} = \rho \) must be imposed, and we have included the magnetic coupling to the particle’s spin \( s \) with \( \gamma \) being the gyromagnetic ratio.

In the next two sections we consider the problem of a many-particle system of charged particles in the presence of an external field produced by some external apparatus. An important task will be to separate out which pieces of the Hamiltonian should be associated with the system and which with the apparatus.

### III. Electrostatics

In this section we neglect the effects of the magnetic field and set

\[ \mathbf{A} = 0 \quad (\text{so } \mathbf{B} = 0), \quad \nabla \times \mathbf{E} = 0, \quad \mathbf{E} = -\nabla \phi, \]

where \( \phi \) is independent of time. We consider a situation in which there is a dielectric which has bound charge density \( \rho_b \) giving rise to an electric field \( \mathbf{E}_b \), as well as free charges \( \rho_{\text{ext}} \), entirely outside the dielectric, which give rise to an external field \( \mathbf{E}_{\text{ext}} \). We have

\[ \rho = \rho_b + \rho_{\text{ext}}, \quad \mathbf{E} = \mathbf{E}_b + \mathbf{E}_{\text{ext}}, \]

and the relation between charge density and corresponding electric field is given by Gauss’ law

\[ \nabla \cdot \mathbf{E} = \rho, \quad \nabla \cdot \mathbf{E}_b = \rho_b, \quad \nabla \cdot \mathbf{E}_{\text{ext}} = \rho_{\text{ext}}. \]

To obtain the Hamiltonian of the dielectric, we remove \( (1/2) \int d\mathbf{x} \mathbf{E}^2_{\text{ext}} \) from Eq. (5), since this is the work done to set up the free charges, and should be considered part of the energy of the external apparatus, not the dielectric. Hence the Hamiltonian of the dielectric is given by

\[ \mathcal{H}_{\text{diele}} = \mathcal{H}_0 + \frac{1}{2} \int d\mathbf{x} \left[ \mathbf{E}^2 - \mathbf{E}_{\text{ext}}^2 \right] \]

\[ = \mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}_2, \]

where \( \mathcal{H}_0 \) is the part of the Hamiltonian not explicitly dependent on the electric field, \( \mathcal{H}_1 \) is given by

\[ \mathcal{H}_1 = \int d\mathbf{x} \mathbf{E}_b \cdot \mathbf{E}_{\text{ext}}, \]

and

\[ \mathcal{H}_2 = \frac{1}{2} \int d\mathbf{x} \mathbf{E}_b^2. \]

Note that there is an implicit dependence of \( \mathcal{H}_0 \) on the electric field because the interactions in \( \mathcal{H}_0 \) depend on the locations of the particles, and these affect the field through Gauss’ law Eq. (5).

It is useful to express Eqs. (11) and (12) in a different way. Writing \( \mathbf{E}_{\text{ext}} = -\nabla \phi_{\text{ext}} \) and integrating by parts, Eq. (11) can be written

\[ \mathcal{H}_1 = \int_V d\mathbf{x} \rho_b \phi_{\text{ext}}, \]

showing that \( \mathcal{H}_1 \) represents the interaction between charges in the dielectric \( \rho_b \) and the external electric potential \( \phi_{\text{ext}} \). The integral in Eq. (13) is only over the volume \( V \) of the sample, and in the rest of this paper we will find it convenient to indicate integrals restricted to the volume of the sample by a subscript \( V \). Integrals with no such indicator will be over all space. Similarly Eq. (12) can be written

\[ \mathcal{H}_2 = \frac{1}{2} \int_V d\mathbf{x} \rho_b \phi_{\text{ext}} \]

\[ = \frac{1}{2} \int_V d\mathbf{x} \int_V d\mathbf{x}' \frac{\rho_b(x_1) \rho_b(x_2)}{4\pi |x_1 - x_2|}, \]

showing that \( \mathcal{H}_2 \) represents the self-interaction of charges in the dielectric. In the second expression in Eq. (14) we used Coulomb’s law.

It is conventional to describe the response of a dielectric to an external field by its polarization \( \mathbf{P} \), satisfying \( \nabla \cdot \mathbf{P} = -\rho_b \). The “electric displacement field” is defined by \( \mathbf{D} = \mathbf{E} + \mathbf{P} \), so that \( \nabla \cdot \mathbf{D} = \rho_{\text{ext}} \). Now any vector field (with appropriate boundary conditions at infinity) can be written as the sum of a longitudinal part (which has zero curl) and a transverse part (which has zero divergence). Comparing the equations for \( \nabla \cdot \mathbf{P} \) and \( \nabla \cdot \mathbf{D} \) with Eq. (8), we have

\[ \mathbf{P}^L = -\mathbf{E}_b, \quad \mathbf{D}^L = \mathbf{E}_{\text{ext}}, \]

where \( \mathbf{P}^L \) and \( \mathbf{D}^L \) are the longitudinal parts of \( \mathbf{P} \) and \( \mathbf{D} \) respectively. However, \( \mathbf{P} \neq -\mathbf{E}_b \) (and \( \mathbf{D} \neq \mathbf{E}_{\text{ext}} \)) because \( \mathbf{P} \) also has a transverse component \( \mathbf{P}^T \), whereas the electric field is purely longitudinal since \( \nabla \times \mathbf{E} = 0 \) in an electrostatic situation. Note that even with the physical condition that \( \mathbf{P} \) must vanish outside the material, \( \mathbf{P}^T \) is ambiguous, although it does not result in any (bound) charges and hence has no measurable consequences. If the polarization is a local effect, with dipole moments being induced in response to the local electric field, one can impose the additional condition \( \mathbf{P} = f(\mathbf{E}) \) (in the simplest case, a linear function) to determine the polarization uniquely. However, when polarization is a non-local process, e.g., in a conductor, it is genuinely ambiguous. For example, for an infinitely long cylindrical conductor of radius \( a \), one can add an azimuthal polarization depending only on \( r \) [i.e., \( P_\theta = \text{const.} g(r) \) for \( 0 < r < a \) and \( P_\theta = 0 \) for \( r > a \)], without changing the electric field.

Now the integral over all space of the product of a longitudinal field and a transverse field is zero, which
is easily proved by writing the longitudinal field as the gradient of a scalar potential and integrating by parts. Hence, since $P = 0$ outside the sample,

$$
\int_V d\mathbf{x} \cdot \mathbf{P} \cdot \mathbf{E}_{\text{ext}} = \int_V d\mathbf{x} \mathbf{P} \cdot \mathbf{E}_{\text{ext}} = \int_V d\mathbf{x} \mathbf{P}_L \cdot \mathbf{E}_{\text{ext}}
$$

$$
= -\int_V d\mathbf{x} \mathbf{E}_b \cdot \mathbf{E}_{\text{ext}} .
$$

Consequently $H_1$ in Eq. (11) can be reexpressed as

$$
H_1 = -\int_V d\mathbf{x} \mathbf{P} \cdot \mathbf{E}_{\text{ext}} .
$$

Hence, putting all this together the Hamiltonian of the dielectric is given by

$$
H_{\text{d}i\text{e}l} = H_0 - \int_V d\mathbf{x} \mathbf{P} \cdot \mathbf{E}_{\text{ext}} + \frac{1}{2} \int_V d\mathbf{x}_1 \int_V d\mathbf{x}_2 \frac{\rho_0(\mathbf{x}_1) \rho_0(\mathbf{x}_2)}{4\pi |\mathbf{x}_1 - \mathbf{x}_2|} .
$$

The free energy is then given by

$$
F_{\text{d}i\text{e}l} = -k_B T \ln \text{Tr} e^{-\beta H_{\text{d}i\text{e}l}} ,
$$

where the trace is over the states of the system.

In equilibrium, the free energy is minimized with respect to $\rho_0$. Let us now change the external field by some small amount $\delta \mathbf{E}_{\text{ext}}$. The bound charges will respond but this causes no change in $F_{\text{d}i\text{e}l}$ to first order because $F_{\text{d}i\text{e}l}$ is at a minimum with respect to $\rho_0$. Hence the change in $F_{\text{d}i\text{e}l}$ comes entirely from the dependence of $H_1$ on $\mathbf{E}_{\text{ext}}$, (see Eq. (17)) which gives

$$
\delta F_{\text{d}i\text{e}l} = -\int_V d\mathbf{x} \mathbf{P} \cdot \delta \mathbf{E}_{\text{ext}} ,
$$

which is a thermodynamic definition of the polarization. The integral, is, of course, only over the sample, not all space, because $\mathbf{P}$ is only non-zero in the sample. If instead one moves the dielectric with $\mathbf{E}_{\text{ext}}$ fixed, Eq. (20) computed in the reference frame of the dielectric also gives the work done in moving the dielectric.

In situations where $\mathbf{P}(\mathbf{x})$ cannot be defined unambiguously, it may be more convenient to replace $\mathbf{P}$ by $-\mathbf{E}_b$ and integrate over all space.

Frequently, e.g. Pippard, a different result for the change in free energy is given, but this corresponds to a different free energy which omits the piece $H_1$ of the Hamiltonian, the interaction between the dipole moment of the system and the external field. Denoting the modified Hamiltonian by $H'_{\text{d}i\text{e}l}$ we have

$$
H'_{\text{d}i\text{e}l} = H_0 + \frac{1}{2} \int d\mathbf{x} \mathbf{E}_b^2 ,
$$

which consists of all terms that do not explicitly involve the external electric field. Now $H_{\text{d}i\text{e}l} - H'_{\text{d}i\text{e}l} = -\int_V d\mathbf{x} \mathbf{P} \cdot \mathbf{E}_{\text{ext}}$, and the relationship between $F_{\text{d}i\text{e}l}$ and $F'_{\text{d}i\text{e}l}$ is the same,

$$
F_{\text{d}i\text{e}l} = F'_{\text{d}i\text{e}l} - \int_V d\mathbf{x} \mathbf{P} \cdot \mathbf{E}_{\text{ext}} ,
$$

i.e. a standard Legendre transformation, and so, using Eq. (20), we have

$$
\delta F'_{\text{d}i\text{e}l} = \int_V d\mathbf{x} \mathbf{E}_{\text{ext}} \cdot \delta \mathbf{P} .
$$

Thus $F'_{\text{d}i\text{e}l}$ (which depends upon the position of the charges) should be regarded as a function of the polarization $\mathbf{P}$, and its derivative with respect to $\mathbf{P}$ gives the external electric field.

It is also interesting to consider the free energy corresponding to including just the Hamiltonian $H_0$. Similar arguments to those given above yield

$$
\delta F_0 = \int_V d\mathbf{x} \mathbf{E} \cdot \delta \mathbf{P} .
$$

The last free energy that we consider in this section is the combined free energy of the external apparatus and dielectric. From Eq. (5) and Eq. (9), this is given by

$$
F_{\text{c}o\text{mb}} = F_0 + \frac{1}{2} \int d\mathbf{x} \mathbf{E}^2 = F_{\text{d}i\text{e}l} + \frac{1}{2} \int d\mathbf{x} \mathbf{E}_{\text{ext}}^2 .
$$

Using Eq. (20), a small change in the fields gives

$$
\delta F_{\text{c}o\text{mb}} = \int d\mathbf{x} (\mathbf{E}_{\text{ext}} - \mathbf{P}) \cdot \delta \mathbf{E}_{\text{ext}}
$$

$$
\quad = \int d\mathbf{x} (\mathbf{D} - \mathbf{P}) \cdot \delta \mathbf{E}_{\text{ext}} = \int d\mathbf{x} \mathbf{E} \cdot \delta \mathbf{E}_{\text{ext}}
$$

$$
\quad = \int d\mathbf{x} \mathbf{E} \cdot \delta \mathbf{D} .
$$

At the first step, the integral of $\mathbf{P} \cdot \delta \mathbf{E}_{\text{ext}}$ is extended to cover all space. At the second and last steps, we use Eq. (16) and the fact that $\delta \mathbf{E}_{\text{ext}}$ and $\mathbf{E}$ are longitudinal. Equation (20) is the total work done on the free charges in setting up the field in the presence of the dielectric and is the form usually presented in the E&M books such as Jackson or Griffiths.

Eqs. (20), (21), (24) and (26) describe different thermodynamic derivatives in the presence of an electric field, each of which involves a different free energy depending upon which pieces of the electric field energy $(1/2) \int d\mathbf{x} (\mathbf{E}_{\text{ext}}^2 + 2 \mathbf{E}_b \cdot \mathbf{E}_{\text{ext}} + \mathbf{E}_{\text{ext}}^2)$ are included. These are summarized in Table II. When the definition of $\mathbf{P}$, $\delta \mathbf{P}$ and $\mathbf{D}$ are ambiguous, one can replace them with $\mathbf{E}_b$, $\delta \mathbf{E}_b$ and $\mathbf{E}_{\text{ext}}$ respectively in the final column of Table II with the integrals over all space. This is because of Eq. (16) and the fact that $\delta \mathbf{E}_{\text{ext}}$, $\mathbf{E}_{\text{ext}}$ and $\mathbf{E}$ are longitudinal. Of the free energies in Table II, $F_{\text{d}i\text{e}l}$
Free energy change
\[ \delta F \]

Table 1: Different free energies for the electrostatic case. For each entry, the free energy is related to the given Hamiltonian

| Hamiltonian | Free energy change |
|-------------|--------------------|
| \( H_{\text{d}i\text{el}} = H_0 + \frac{1}{2} \int dx (E_b^2 + 2E_b \cdot E_{\text{ext}}) \) | \( \delta F_{\text{d}i\text{el}} = - \int_V dx P \cdot \delta E_{\text{ext}} \) [5] |
| \( H'_{\text{d}i\text{el}} = H_0 + \frac{1}{2} \int dx E_b^2 \) | \( \delta F'_{\text{d}i\text{el}} = \int_V dx E_{\text{ext}} \cdot \delta P \) [5, 7] |
| \( H_{\text{comb}} = H_0 + \frac{1}{2} \int dx (E_b^2 + 2E_b \cdot E_{\text{ext}} + E_{\text{ext}}^2) \) | \( \delta F_{\text{comb}} = \int_V dx E \cdot \delta D \) [3, 4] |
| \( H_0 \) | \( \delta F_0 = \int_V dx E \cdot \delta P \) |

IV. MAGNETOSTATICS

In this section we consider a static magnetic field and so set

\[ E = 0 \], \quad B = \nabla \times A. \] (27)

The “system” is a magnetic material with “bound” current density \( J_b \) producing a magnetic field \( B_b \), and in addition there is a source of external magnetic field \( B_{\text{ext}} \), produced by a “free” current density \( J_{\text{ext}} \) which lies entirely outside the system. We have

\[ J = J_b + J_{\text{ext}}, \quad B = B_b + B_{\text{ext}}. \] (28)

The relation between the current and corresponding magnetic field is given by Ampère’s law,

\[ \nabla \times B = J, \quad \nabla \times B_b = J_b, \quad \nabla \times B_{\text{ext}} = J_{\text{ext}}. \] (29)

As in the previous section, we separate out which terms in the Hamiltonian are part of the material, from those which are part of the external apparatus. For the electrostatic case, the energy needed to create the external field is \((1/2) \int dE_{\text{ext}}^2\), independent of the state of the system, so it was simple to subtract this off to get the Hamiltonian of the material. For the magnetostatic case, the situation is more complicated since a change in the magnetic field produced by the material generates, according to Faraday’s law, a back EMF, \( E \), in the coil producing the external field, and so work has to be done to maintain the external current and field. This work is done at a rate

\[ \frac{dW}{dt} = - \int dx J_{\text{ext}} \cdot E. \] (30)

Using \( \nabla \times E = J_{\text{ext}} \), integrating by parts, and using \( \nabla \times E = -\partial_t B \), we obtain

\[ \delta W = \int dx B_{\text{ext}} \cdot \delta B. \] (31)

Hence the total work done to maintain the external field if the total field increases from 0 to \( B \) (due to changes in the system) is

\[ W = \int dx B_{\text{ext}} \cdot B. \] (32)

This is part of the energy of the external apparatus (since it is that which maintains the external current) and so should be subtracted from the total energy when determining the energy of the system. In addition, we need to subtract the magnetic field energy due entirely to the external field, which is \((1/2) \int dB_{\text{ext}}^2\) from Eq. 3 and \(- \int dx B^2_{\text{ext}}\) from Eq. 32. The net effect of this is to add \((1/2) \int dB_{\text{ext}}^2\).

Hence, from Eq. 3, the Hamiltonian of the magnetic material is

\[ H_{\text{mat}} = H_0 \left( \{ p - qA \} \right) + \frac{1}{2} \int dx (B - B_{\text{ext}})^2. \] (33)

where \( H_0 \left( \{ p - qA \} \right) \) is the Hamiltonian of the material in the absence of a magnetic field except that the momentum \( p \) of a particle is replaced by \( p - qA \) and for each spin \( s \) there is an additional energy \(-sB \cdot B\). (To avoid too cumbersome a notation we do not explicitly indicate the dependence of \( H_0 \) on the spins.)

Whereas the electric field in the electrostatic is not a dynamical variable, but is completely determined by
the charge density, the magnetic field is a dynamical variable. More precisely, to ensure $\nabla \cdot B = 0$, we write $B = \nabla \times A$ and treat $A$ as a dynamical variable in some gauge, e.g. $\nabla \cdot A = 0$ which is known as the Coulomb gauge. The free energy of the magnetic material is given by

$$F_{\text{mat}} = -k_B T \ln \text{Tr} \ e^{-\beta \mathcal{H}_{\text{mat}}},$$

where the trace is over both the state of the system and the vector potential in the Coulomb gauge.

It is conventional to describe the response of a material to a magnetic field by its magnetization $M$, where $\nabla \times M = J_b$ and to define the auxiliary field $H$ as $H = B - M$ so that $\nabla \times H = J_{\text{ext}}$. Analogous to our discussion of polarization in electrostatics, by comparing with Eq. (24) we see that the transverse parts of $M$ and $H$ satisfy

$$M^T = B_b \quad \text{and} \quad H^T = B_{\text{ext}}.$$  

(35)

However, the longitudinal part of $M$ and $H$ are not specified, unless $M$ is a local function of $B$. When the magnetization is a non-local process, as in a superconductor, the definition of the longitudinal part of $M$ is genuinely ambiguous.

Let the external magnetic field $B_{\text{ext}}$ be changed by $\delta B_{\text{ext}} = \nabla \times \delta A_{\text{ext}}$, and calculate the change in free energy. Although $B$ and all parameters of the material will respond to $\delta B_{\text{ext}}$, they cause no change in $F_{\text{mat}}$ to first order (as in the electrostatic case). Therefore

$$\delta F_{\text{mat}} = \int_V \delta B \times A_{\text{ext}}$$

$$= - \int_V dx J_b \cdot \delta A_{\text{ext}}$$

$$= - \int_V dx \ M \cdot \delta B_{\text{ext}},$$

(36)

where the second step used Ampère’s law, Eq. (26), and the third step an integration by parts with $\nabla \times M = J_b$. Equation (36) is given in de Gennes[11] and Kittel[15]. As in the electrostatic case, this expression can also be used to find the work done when moving a magnetic material in an external magnetic field.

Next we discuss other choices that appear in the literature for the Hamiltonian and corresponding free energy. To a good approximation we can replace the trace over the vector potential by the vector potential field which minimizes the free energy. This amounts to ignoring thermal fluctuations in the vector potential, similar to the neglect of quantum fluctuations in the radiation field that is customary in elementary quantum mechanics[12].

Defining $F_0 = -k_B T \ln \text{Tr} \ e^{-\beta \mathcal{H}_0}$ we have

$$\delta F_0 = \delta F_{\text{mat}} - \int_V dx (B - B_{\text{ext}}) \cdot (\delta B - \delta B_{\text{ext}}).$$

(37)

Since $\delta B - \delta B_{\text{ext}}$ is transverse, from Eq. (36) we can replace $B - B_{\text{ext}}$ with $M$. Using Eq. (36), we obtain

$$\delta F_0 = - \int_V dx \ M \cdot \delta B$$

(38)

which can be used as the thermodynamic definition of the magnetization.

Some authors, e.g. Callen[13] and Pippard[7], take the Hamiltonian of the system to be

$$\mathcal{H}'_{\text{mat}} = \mathcal{H}_0 \{\mathcal{P} - q A\} + \frac{1}{2} \int \delta \mathbf{B}^2$$

(39)

rather than Eq. (35). Equation (39) counts the energy to initially set up the magnetic field, $(1/2) \int \delta \mathbf{B}^2$, to be part the external apparatus, but the work done by the external currents to maintain the external field (if some change is made to the magnetic material) is regarded as energy of the material. Comparing Eq. (39) with Eq. (35), and using Eq. (36), one can see that the free energy $F_{\text{mat}}' \propto \delta \mathcal{H}'_{\text{mat}}$ is given by

$$F_{\text{mat}} = F_{\text{mat}}' - \int_V dx \ M \cdot \delta B_{\text{ext}}.$$ 

(40)

Hence, from Eq. (30), we have

$$dF_{\text{mat}} = \int_V dx B_{\text{ext}} \cdot \delta M.$$ 

(41)

The last free energy we consider in this section, is the combined free energy of the external apparatus and the magnetic material. From Eq. (35) this is given by

$$F_{\text{comb}} = F_0 + \frac{1}{2} \int V \delta \mathbf{B}^2.$$ 

(42)

From Eq. (35) a small change in the fields gives

$$\delta F_{\text{comb}} = \int V \delta \mathbf{B} \cdot \delta \mathbf{B} = \int V \delta \mathbf{B} \cdot \delta \mathbf{B}.$$ 

(43)

Equation (43) is the result given in the E&M books such as Jackson[3].

Eqs. (36), (38), (41) and (43) describe different thermodynamic derivatives in the presence of an magnetic field, each of which involves a different free energy depending upon which pieces of the magnetic field energy $(1/2) \int \delta \mathbf{B}^2 + 2B_b \cdot B_{\text{ext}} + B_{\text{ext}}^2$ are included. These are summarized in Table III. In situations where the definition of $M$ (and hence $H$) is ambiguous one can replace $M$, $\delta M$ and $H$ with $B_b$, $\delta B_b$ and $B_{\text{ext}}$, respectively in the last column of Table III after extending the integrals to cover all space. This relies on Eq. (35) and the fact that $B_{\text{ext}}$, $B_{\text{ext}}$ and $\delta B$ are transverse. Of the free energies in Table III $F_{\text{mat}}$ is the most useful since it...
includes everything associated with the magnetic material: (i) the part of the Hamiltonian not involving the magnetic field (except that we replace \( p \rightarrow p - qA \) and add \(-\gamma s \cdot B\) for each spin) and (ii) the long-range dipole-dipole interaction between magnetic moments in the material.

V. CONCLUSIONS

The main results of the paper are summarized in Tables IX and XI. For statistical mechanics applications, we have argued that the most appropriate Hamiltonian for the system (neglecting the Hamiltonian of the external apparatus) is the first line of these tables, i.e.

\[
\mathcal{H}_{\text{dil}} = \mathcal{H}_0 + \frac{1}{2} \int d\mathbf{x} \left[ \mathbf{E}^2 - \mathbf{E}_{\text{ext}}^2 \right] \tag{44}
\]

for the electric case and

\[
\mathcal{H}_{\text{mat}} = \mathcal{H}_0 (\{p - qA\}) + \frac{1}{2} \int d\mathbf{x} (\mathbf{B} - \mathbf{B}_{\text{ext}})^2. \tag{45}
\]

for the magnetic case. The corresponding free energy changes are

\[
\delta F_{\text{dil}} = -\int_V d\mathbf{x} \mathbf{P} \cdot \mathbf{E}_{\text{ext}} \tag{46}
\]

and

\[
\delta F_{\text{mat}} = -\int_V d\mathbf{x} \mathbf{M} \cdot \mathbf{B}_{\text{ext}}. \tag{47}
\]

The relation between the first line of the tables and the second is given, in each case, by a standard Legendre transform, see Eqs. (22) and (30). Unfortunately, Eqs. (10) and (17) do not figure prominently in statistical mechanics textbooks. Reference 5 is a notable exception, but unfortunately is not in print. By contrast, for problems in electricity and magnetism we are generally interested in the total work done (on the free charges and currents), which is given by the third line of the tables, and fortunately, these are the results quoted in E&M books.

It is interesting to note that although the final results for the free energy changes in the electric and magnetic cases are exactly analogous to each other, there are differences in the Hamiltonians from which these results are derived. The first difference is that the field energy involves \( (1/2) \int d\mathbf{x} (\mathbf{E}^2 - \mathbf{E}_{\text{ext}}^2) = \int d\mathbf{x} (\mathbf{E}^2_{\text{ext}} - \mathbf{E}_{\text{ext}} \cdot \mathbf{E}_{\text{ext}}) \) in the electric case as opposed to \( (1/2) \int d\mathbf{x} (\mathbf{B} - \mathbf{B}_{\text{ext}})^2 = (1/2) \int d\mathbf{x} \mathbf{B}_{\text{ext}}^2 \) in the magnetic case, \( \int d\mathbf{x} (\mathbf{B}_{\text{ext}}^2 - \mathbf{B}_{\text{ext}} \cdot \mathbf{B}_{\text{ext}}) \), comes from the work done by the external sources in the magnetic case to maintain the external currents against the back EMF produced by a change in the field of the system. The second difference is that whereas \( \mathcal{H}_0 \) does not have an explicit dependence on the electric field (though it depends on it implicitly, since \( \mathbf{E} \) is tied to the charge density through Gauss’s law, Eq. (11)), it does depend explicitly on the magnetic field, since one has to replace the velocity \( \mathbf{x} \) by \( \mathbf{p} - q\mathbf{A} \) where \( \mathbf{p} \) is the canonical momentum.

For the case of magnetism due to spins, \( s_i \), there is also an explicit interaction \(-\gamma \sum_i s_i \cdot \mathbf{B} \) in \( \mathcal{H}_0 \). Classically, one can change variables from \( \mathbf{p} \) to \( \mathbf{p}' = \mathbf{p} - q\mathbf{A} \), there is no spin magnetism, and the field energy only involves \( \mathbf{B}_b \), so there is no magnetism\footnote{Reference 10}. However, since in quantum mechanics there are constraints on \( \mathbf{p} \) and not \( \mathbf{p}' \), for example that the angular momentum \( \mathbf{r} \times \mathbf{p} \) must be a multiple of \( h \), there is a coupling between the dipole moment of the material and the external field from the \( \mathcal{H}_0(\{p - qA\}) \) part — or the spin term — of the Hamiltonian.

It is useful to compare the equilibrium free energies we have discussed so far with the Landau free energy function which forms the basis of Landau’s theory of second order phase transitions\footnote{Reference 12}, and which is applicable away from equilibrium. The partition function, required in evaluating the free energy through statisti-
cal mechanics, is written (for the magnetic case) as

\[ Z(B_{\text{ext}}) = \sum_m \text{Tr} \exp\left[-\beta F_L(m, B_{\text{ext}})\right], \]

where \( \text{Tr} \) is a restricted trace, carried out over states with a specified value of total magnetic moment \( m \), and the Landau free energy \( F_L \) is defined through this equation. In Eq. (48), the sum is dominated by the value of \( m \) which minimizes \( F_L \) at fixed \( B_{\text{ext}} \) (assumed independent of \( x \) here); this is the equilibrium magnetization at \( B_{\text{ext}} \). Denoting this equilibrium value of \( m \) by \( m^* \), we have

\[ F_L(m^*, B_{\text{ext}}) = F_{\text{mat}}(B_{\text{ext}}). \]  

(49)

For the case of spin magnetism, Eq. (48) simplifies further. As seen in Eq. (4), the coupling between the external field and the system occurs only through the term \(-m \cdot B_{\text{ext}}\), \( (m = \gamma \sum_i s_i) \), the part of \(-m \cdot B\) involving the external field. Therefore

\[ F_L(m, B_{\text{ext}}) = F(m) - m \cdot B_{\text{ext}} \]  

(50)

where \( F(m) \) does not depend on the externally applied magnetic field. In this case, comparing with Eq. (49) we see that

\[ F(m) = F_{\text{mat}}. \]  

(51)

A similar process can also be carried out for the electrostatic case, since the coupling term in \( \mathcal{H}_{\text{dier}} \) is

\[ -\int d\mathbf{x} \mathbf{E}_b \cdot \mathbf{E}_{\text{ext}} = -\int d\mathbf{x} \mathbf{P} \cdot \mathbf{E}_{\text{ext}}. \]  

However, for orbital magnetism, \( B_{\text{ext}} \) cannot be separated out cleanly like this due to the diamagnetic term, and one is limited to Eq. (48) if the diamagnetic contribution is significant.

Finally, we observe that the ‘external’ parts of the Hamiltonian, that were discarded in going from Eq. (17) to Eqs. (18) and (19), were \((1/2) \int d\mathbf{x} \mathbf{E}_{\text{ext}}^2\) and \(-(1/2) \int d\mathbf{x} \mathbf{B}_{\text{ext}}^2\). The sign reversal between the two leads to the well known result that free charges move to minimize the energy of the electric field (the position of the charges in a conductor can be viewed as such a minimization problem, with constraints) whereas loops carrying free current (held constant by batteries) move to maximize the energy stored in the magnetic field.

We hope that a brief discussion of the points discussed here will eventually find their way into textbooks on statistical mechanics so that future students will be less confused about the free energy of a system in an electric or magnetic field than were the authors of this paper.

We would like to thank D. Belanger for a critical reading of the manuscript.

---

* Electronic address: narayan@physics.ucsc.edu

1 It is difficult to find a single text which derives both Maxwell’s equations and the Lorentz force from the Lagrangian in Eq. (1). However Shankar obtains the Lorentz force, and Jackson obtains Maxwell’s equations (in relativistic notation).

2 R. Shankar, *Principles of Quantum Mechanics* (Kluwer, New York, NY, 1999), 2nd ed., p. 84.

3 J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, NY, 1999), 3rd ed., pp. 598–600, pp. 241–242, pp. 165–166, pp. 212–213.

4 D. J. Griffiths, *Introduction to Electrodynamics* (Prentice-Hall, Englewood Cliffs, NJ, 1989), 3rd ed., pp. 52–53, pp. 191–192, Appendix B.

5 C. Kittel, *Thermal Physics*, (Wiley, New York, 1969), 1st ed., Ch. 22, Ch. 23, Appendix F. This text gives a good discussion of the different free energies in electric and magnetic fields, although the results for the magnetic field are given “by analogy”, which (as discussed in the final section of this paper) is hazardous. It is unfortunate that this material is omitted from the second edition.

6 C. Kittel and H. Kroemer, *Thermal Physics*, (Wiley, New York, 1980), 2nd ed.

7 A. B. Pippard, *Classical Thermodynamics* (Cambridge University Press, London, 1966), pp. 26–27.

8 H. Bokil and O. Narayan, “Flux penetration in slab-shaped type-I superconductors”, Phys. Rev. B 56, 11195–1200 (1997).

9 D. S. Fisher, M. P. A. Fisher and D. A. Huse, “Thermal fluctuations, quenched disorder, phase transitions, and transport in type-II superconductors”, Phys. Rev. B 43, 130–159 (1991).

10 L. D. Landau, E. M. Lifshitz and L. P. Pitaevskii, *Electrodynamics of Continuous Media* (Pergamon, New York, NY, 1984), p. 181.

11 P. G. de Gennes, *Superconductivity of Metals and Alloys* (Addison-Wesley Redwood City, CA, 1989), p. 33–34 especially Eq. (2.45).

12 H. A. Bethe and R. Jackiw, *Intermediate Quantum Mechanics* (Addison-Wesley, Reading, MA, 1997), p. 193.

13 H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics* (Wiley, New York, NY, 1985), 2nd ed., Appendix B.

14 There does not seem to be any standard notation for the free energies that we call \( F_{\text{mat}} \) and \( F'_{\text{mat}} \). For example Kittel calls them \( F_A \) and \( F_B \). Some authors use the terms “Gibbs” and “Helmholtz” free energies, but we
prefer to reserve these terms for free energies which differ by a factor of $PV$.

15 N. Bohr, Dissertation, Copenhagen (1911); J. H. Van Leeuwen, J. Phys. (Paris), 2, 361 (1921).

16 L. D. Landau and E. M. Lifshitz, *Statistical Mechanics* (Pergamon, New York, NY, 1969), 2nd ed., Ch. 14.

17 S.-K. Ma, *Statistical Mechanics* (World Scientific, Singapore, 1985), §27.3.

18 R. P. Feynman, R. B. Leighton and M. Sands, *The Feynman Lectures on Physics* (Addison-Wesley, Reading MA, 1964), vol. 2, Eq. 17.39, §17-8.