

*“The essential idea is that in the  $N \rightarrow \infty$  limit of large systems (on our own macroscopic scale) it is not only convenient but essential to realize that matter will undergo mathematically sharp, singular phase transitions to states in which the microscopic symmetries, and even the microscopic equations of motion, are in a sense violated. The symmetry leaves behind as its expression only certain characteristic behaviors.”*

*P W Anderson, “More is Different,” Science **177**, 393 (1972).*

## Chapter 12

# *Thermodynamics and Magnetism*

### 12.1 *Magnetism in Solids*

Lodestones – fragments of magnetic<sup>1</sup>  $FeO + Fe_2O_3$  ( $Fe_3O_4$ ) – although known to the ancients were, according to Pliny the Elder, first formally described in Greek 6<sup>th</sup> century B.C.E. writings. By that time they were already the stuff of myth, superstition and amazing curative claims, some of which survive to this day. The Chinese used lodestones in navigation as early as 200 B.C.E and are credited with inventing the magnetic compass in the 12th century AD.

Only in the modern era has magnetism become well understood, inspiring countless papers, books<sup>2</sup> and more than a dozen Nobel prizes in both fundamental and applied research. Among the forms of macroscopic magnetism are:

1. **Paramagnetism:** In an external magnetic field  $\mathcal{B}$  the spin-state degeneracy

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<sup>1</sup>Named, as one story goes, for Magnus, the Greek shepherd who reported a field of stones that drew the nails from his sandals.

<sup>2</sup>See e.g. Stephen Blundell, “Magnetism in Condensed Matter” Oxford Maser Series in Condensed Matter Physics (2002); Daniel C Mattis, “Theory of Magnetism Made Simple,” World Scientific, London (2006); Robert M. White, “Quantum Theory of Magnetism: Magnetic Properties of Materials,” 3rd rev. ed., Springer-Verlag, Berlin (2007).

of local (atomic) or itinerant (conduction) electronic states is lifted (Zeeman effect). At low temperature this results in an induced macroscopic magnetic moment whose vector direction lies parallel to the external field. This is referred to as *paramagnetism*.<sup>3</sup>

For most materials removing the external field restores spin-state degeneracy, returning the net moment to zero.

2. **Diamagnetism:** Macroscopic magnetization may also be induced with a magnetization vector *anti-parallel* to the external field, an effect called diamagnetism. In conductors diamagnetism arises from the highly degenerate quantum eigen-energies and eigenstates (referred to as *Landau levels*.)<sup>4</sup> formed by interaction between mobile electrons and magnetic fields. Diamagnetism is also found in insulators, but largely from surface quantum orbitals rather than interior bulk states.<sup>5</sup> Both cases are purely quantum phenomena, leaving macroscopic diamagnetism without an elementary explanatory model.<sup>6,7</sup> All solids show some diamagnetic response, but it is usually dominated by any paramagnetism that may be present.

At high magnetic fields and low temperatures very pure metals exhibit an *oscillatory diamagnetism* called the de Haas-van Alfen effect whose source is exclusively the Landau levels.<sup>8</sup>

### 3. Permanent Magnetism

- **Ferromagnetism:** Ferromagnetism is an ordered state of matter in which local paramagnetic moments interact to produce an *effective internal magnetic field* with collective alignment of moments throughout distinct regions called domains. Due to these internal interactions, domains *can remain aligned* even after the external field is removed.

Ferromagnetic alignment “abruptly” disappears above a material specific temperature called the Curie temperature  $T_c$ , at which point ordinary local para-

<sup>3</sup>Itinerant (conduction) electron paramagnetism is referred to as spin or Pauli paramagnetism.

<sup>4</sup>L. Landau “Diamagnetism of Metals,” Z. Phys. **64**, 629 (1930).

<sup>5</sup>D. Ceresoli, et. al. “Orbital magnetization in crystalline solids,” Phys. Rev. B **74**, 24408 (2006).

<sup>6</sup>Niels Bohr, “Studier over Metallernes Elektrontheori,” Kbenhavns Universitet (1911).

<sup>7</sup>Hendrika Johanna van Leeuwen, “Problmes de la thorie lectronique du magnatisme,” Journal de Physique et le Radium, **2** 361 (1921).

<sup>8</sup>D. Shoenberg, “Magnetic Oscillations in Metals,” Cambridge University Press, Cambridge (1984).

magnetism reasserts.

- **Antiferromagnetism:** At low temperatures, interactions between adjacent *identical* paramagnetic atoms, ions or sub-lattices can induce “anti-alignment” of adjacent paramagnets, resulting in a net *zero* magnetic moment.
- **Ferrimagnetism:** At low temperatures interactions between *unequivalent* paramagnetic atoms, ions or sub-lattices can produce “anti-alignment” of moments, resulting in a *small* residual magnetization.

In both ferrimagnetism and antiferromagnetism increasing temperature weakens “anti-alignment” with the collective *induced* moments approaching a maximum. Then, at a material specific temperature called the *Néel* temperature  $T_N$ , anti-alignment disappears and the materials becomes paramagnetic.

In this chapter general concepts in the thermodynamics of magnetism and magnetic fields are discussed as well as models of local paramagnetism and ferromagnetism.

### 12.1.1 *Magnetic Work*

Central to integrating magnetic fields and magnetizable systems into the *First Law of Thermodynamics* is a formulation of magnetic work. Using Maxwell’s fields,<sup>9</sup> the energy generated within a volume  $V$  in a time  $\delta t$ , by an electric field  $\mathcal{E}$  acting on true charge currents  $\mathcal{J}$  – *Joule Heat* – is<sup>10</sup>

$$\delta W^M = -\delta t \int_V \mathcal{J} \cdot \mathcal{E} dV . \quad (12.1)$$

Therefore the *quasi-static and reversible*<sup>11</sup> magnetic work done by the system is

$$\delta W_{QS}^M = \delta t \int_V \mathcal{J} \cdot \mathcal{E} dV . \quad (12.2)$$

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<sup>9</sup>Maxwell fields in matter and free space are the local averages that appear in his equations of electromagnetism.

<sup>10</sup>Since heat and work are not state functions they do not have true differentials, so the wiggly  $\delta$ 's are used instead to represent incremental work in an interval of time  $\delta t$ .

<sup>11</sup>In specifying reversibility non-reversible hysteresis effects are excluded.

Using Maxwell's Equation (in cgs-Gaussian units)<sup>12</sup>

$$\nabla \times \mathcal{H} = \frac{4\pi}{c} \mathcal{J} + \frac{1}{c} \frac{\delta \mathcal{D}}{\delta t} \quad (12.3)$$

the work done **by** the system is

$$\delta \mathcal{W}_{QS}^M = \delta t \left\{ \frac{c}{4\pi} \int_V (\nabla \times \mathcal{H}) \cdot \mathcal{E} \, dV - \frac{1}{4\pi} \int_V \frac{\delta \mathcal{D}}{\delta t} \cdot \mathcal{E} \, dV \right\}. \quad (12.4)$$

Using the vector identity

$$U \cdot \nabla \times V = \nabla \cdot (V \times U) + V \cdot \nabla \times U \quad (12.5)$$

this becomes

$$\delta \mathcal{W}_{QS}^M = \delta t \left\{ \frac{c}{4\pi} \left[ \int_V \nabla \cdot (\mathcal{H} \times \mathcal{E}) \, dV + \int_V \mathcal{H} \cdot \nabla \times \mathcal{E} \, dV \right] - \frac{1}{4\pi} \int_V \frac{\delta \mathcal{D}}{\delta t} \cdot \mathcal{E} \, dV \right\}. \quad (12.6)$$

The first integral on the right can be transformed by Gauss' theorem into a surface integral. But since the fields are static (non-radiative), they fall off faster than  $\frac{1}{r^2}$  so that for a very distant surface the surface integral can be neglected. Then, with the Maxwell Equation (Faraday's Law)

$$\nabla \times \mathcal{E} = -\frac{1}{c} \left( \frac{\delta \mathcal{B}}{\delta t} \right) \quad (12.7)$$

incremental work done **by** the system is

$$\delta \mathcal{W}_{QS}^M = -\delta t \left\{ \frac{1}{4\pi} \int_V \mathcal{H} \cdot \frac{\delta \mathcal{B}}{\delta t} \, dV + \frac{1}{4\pi} \int_V \frac{\delta \mathcal{D}}{\delta t} \cdot \mathcal{E} \, dV \right\} \quad (12.8)$$

$$= - \left\{ \frac{1}{4\pi} \int_V \mathcal{H} \cdot \delta \mathcal{B} \, dV + \frac{1}{4\pi} \int_V \delta \mathcal{D} \cdot \mathcal{E} \, dV \right\}, \quad (12.9)$$

where the integrals are over the volume of the sample *and* surrounding free space.

**Note:** The fields are functions of the coordinates  $\mathbf{x}$  and are not just simple variables,

<sup>12</sup>Although cgs units have fallen out of pedagogical favor in newer text books, they offer unrivaled clarity in presenting the subtle issues involved in thermodynamics of magnetic and electric fields.

so that here the “wiggly” deltas in  $\delta\mathcal{B}(\mathbf{x})$  and  $\delta\mathcal{H}(\mathbf{x})$  represent *functional* changes, i.e. changes in the *fields* not the coordinates.

Limiting the discussion to magnetic phenomena, the magnetic contribution to *quasi-static* work done by the system is therefore

$$\delta\mathcal{W}_{QS}^M = - \left\{ \frac{1}{4\pi} \int_V \mathcal{H} \cdot \delta\mathcal{B} \, dV \right\}, \quad (12.10)$$

so that the thermodynamic identity becomes

$$\delta\mathcal{U} = T\delta\mathcal{S} - p \, dV + \frac{1}{4\pi} \int_V \mathcal{H} \cdot \delta\mathcal{B} \, dV. \quad (12.11)$$

From the Helmholtz potential, defined as  $F = \mathcal{U} - T\mathcal{S}$ ,

$$\delta F = \delta\mathcal{U} - T\delta\mathcal{S} - \mathcal{S} \, dT, \quad (12.12)$$

which when combined with Eq.12.11 gives the change  $\delta F$

$$\delta F = -\mathcal{S} \, dT - p \, dV + \frac{1}{4\pi} \int_V \mathcal{H} \cdot \delta\mathcal{B} \, dV. \quad (12.13)$$

Defining a magnetic enthalpy  $H$  as

$$H = \mathcal{U} + pV - \frac{1}{4\pi} \int_V \mathcal{B} \cdot \mathcal{H} \, dV, \quad (12.14)$$

gives, using Eq.12.11, an enthalpy change  $\delta H$

$$\delta H = T\delta\mathcal{S} + V \, dp - \frac{1}{4\pi} \int_V \mathcal{B} \cdot \delta\mathcal{H} \, dV. \quad (12.15)$$

Finally, a magnetic Gibbs potential  $G$  is defined as

$$G = F + pV - \frac{1}{4\pi} \int_V \mathcal{B} \cdot \mathcal{H} \, dV, \quad (12.16)$$

which with Eq.12.13 gives the Gibbs potential change  $\delta G$

$$\delta G = -\mathcal{S} dT + V dp - \frac{1}{4\pi} \int_V \mathcal{B} \cdot \delta \mathcal{H} dV. \quad (12.17)$$

Magnetization density<sup>13</sup>  $\mathcal{M}$  and polarization density<sup>14</sup>  $P$  are introduced by the linear constitutive relations

$$\mathcal{H} = \mathcal{B} - 4\pi\mathcal{M} \quad (12.18)$$

and

$$\mathcal{D} = \mathcal{E} + 4\pi P \quad (12.19)$$

in which case *quasi-static* magnetic work may be written

$$\delta \mathcal{W}_{QS}^{\mathcal{M}^1} = \left\{ \frac{1}{4\pi} \int_V \mathcal{B} \cdot \delta \mathcal{B} dV - \int_{V'} \mathcal{M} \cdot \delta \mathcal{B} dV \right\} \quad (12.20)$$

or

$$\delta \mathcal{W}_{QS}^{\mathcal{M}^2} = \left\{ \frac{1}{4\pi} \int_V \mathcal{H} \cdot \delta \mathcal{H} dV + \int_{V'} \mathcal{H} \cdot \delta \mathcal{M} dV \right\}, \quad (12.21)$$

while *quasi-static* electric work may be written

$$\delta \mathcal{W}_{QS}^{P^1} = \left\{ \frac{-1}{4\pi} \int_V \mathcal{D} \cdot \delta \mathcal{D} dV + \int_{V'} P \cdot \delta \mathcal{D} dV \right\} \quad (12.22)$$

or

$$\delta \mathcal{W}_{QS}^{P^2} = \left\{ \frac{-1}{4\pi} \int_V \mathcal{E} \cdot \delta \mathcal{E} dV - \int_{V'} \mathcal{E} \cdot \delta P dV \right\}. \quad (12.23)$$

Both alternatives have, as the first term, total field energies – integrals over all space, both inside and outside matter. The second terms are integrals only *over  $V'$  which*

<sup>13</sup>Total magnetic moment per unit volume.

<sup>14</sup>total electric dipole moment per unit volume

*includes just the volume of magnetized (polarized) matter.* Since magnetic (electric) thermodynamics is primarily concerned with magnetized (polarized) matter, one practice is to bravely ignore the total field energies completely. Another is to absorb the field energies into the internal energy  $\mathcal{U}$ . But since neither option is entirely satisfactory a third way is discussed below, in Subsection 12.1.2.

Nevertheless, these results – in terms of *local average fields* – are general and thermodynamically correct.<sup>15</sup> But they are not convenient to apply. Nor are they the fields that appear in a microscopic magnetic (electric) quantum hamiltonian. In quantum magnetic (electric) models the hamiltonians for individual magnetic (electric) moments depend only on the *local*  $\mathcal{B}$  (*local*  $\mathcal{E}$ ) fields in which the *individual particles move*. In the absence of internal currents or inter-particle interactions, this is the same as the *external (applied) field*  $\mathcal{B}_0$  ( $\mathcal{E}_0$ ) – *the field before the sample is introduced*. After the sample is introduced, *internal fields* can additionally result from:

- a. Interactions between induced moments which are accounted for by additional terms in the hamiltonian. These interactions may be reducible to “effective internal fields” [see, for example, Subsection 12.1.5, below],
- b. Internal “demagnetizing” fields arising from fictitious surface “poles” induced by  $\mathcal{B}_0$ ,<sup>16</sup>
- c. Internal currents induced by the applied field (especially in conductors).<sup>17</sup>

### 12.1.2 *Microscopic Models and Uniform Fields*

Therefore, in microscopic models magnetic and electric hamiltonians are expressed in terms of *uniform applied fields* ( $\mathcal{B}_0$ ,  $\mathcal{E}_0$ ) present *before* matter is introduced. This emphasis on *applied fields* (rather than average Maxwell fields within matter) results in thermodynamic relations somewhat different from Eqs.12.11 - 12.17 above. Again focusing on magnetic effects, in the absence of internal magnetic interactions, *quasi-static magnetic work* done **by** the system is [see Eq.12.54 in Appendix G],

$$d\mathcal{W}_{QS}^M = -\mathcal{B}_0 \cdot d\mathbf{M} \quad (12.24)$$

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<sup>15</sup>The second of these  $\delta\mathcal{W}_{QS}^M$  has the correct form for work, *intensive*  $\times$  *extensive*.

<sup>16</sup>Which introduces sample shape dependence into the magnetic properties.

<sup>17</sup>T Holstein, RE Norton and P Pincus, ”de Haas-van Alphen Effect and the Specific Heat of an Electron Gas,” Physical Review **B** 8 2649 (1973).

so that thermodynamic differential relations become [see Eqs.??, ??, ?? and ??]

$$T d\mathcal{S} = d\mathcal{U}^* + p dV - \mathcal{B}_0 \cdot d\mathbf{M} \quad (12.25)$$

$$T d\mathcal{S} = dH^* - V dp + \mathbf{M} \cdot d\mathcal{B}_0 \quad (12.26)$$

$$dF^* = -\mathcal{S}dT - p dV + \mathcal{B}_0 \cdot d\mathbf{M} \quad (12.27)$$

$$dG^* = -\mathcal{S} dT + V dp - \mathbf{M} \cdot d\mathcal{B}_0 \quad (12.28)$$

where the starred potentials are

$$\mathcal{U}^* = \mathcal{U} + \frac{1}{8\pi} \int_V \mathcal{B}_0^2 dV, \quad (12.29)$$

$$H^* = H + \frac{1}{8\pi} \int_V \mathcal{B}_0^2 dV, \quad (12.30)$$

$$F^* = F + \frac{1}{8\pi} \int_V \mathcal{B}_0^2 dV, \quad (12.31)$$

$$G^* = G + \frac{1}{8\pi} \int_V \mathcal{B}_0^2 dV. \quad (12.32)$$

With  $\mathcal{B}_0$  uniform a *total macroscopic magnetization vector*  $\mathbf{M}$  has been defined:

$$\mathbf{M} = \int_{V'} \langle \mathcal{M} \rangle dV, \quad (12.33)$$

with  $\langle \mathcal{M} \rangle$  the average magnetization per unit volume.<sup>18</sup>

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<sup>18</sup>Similarly

$$d\mathcal{W}_{QS}^P = \mathcal{E}_0 \cdot d\mathbf{P}. \quad (12.34)$$



### 12.1.3 Local Paramagnetism

The classical energy of a magnetic moment  $\mathbf{m}$  in an average local (Maxwell) magnetic field  $\mathcal{B}$  is

$$E = -\mathbf{m} \cdot \mathcal{B}. \quad (12.35)$$

Fundamental particles (electrons, protons, neutrons, etc.) all have intrinsic magnetic moments for which quantum mechanics postulates an operator replacement  $\mathbf{m} \rightarrow \mathbf{m}_{op}$ , and a quantum paramagnetic hamiltonian

$$\mathcal{H}_M = -\mathbf{m}_{op} \cdot \mathcal{B}_0. \quad (12.36)$$

Here  $\mathcal{B}_0$  is the *uniform field* present *before* matter is introduced.<sup>19</sup>

The paramagnetic hamiltonian for a solid consisting of  $N$  identical atoms fixed at crystalline sites  $i$  is

$$\mathcal{H} = \mathcal{H}_0 - \mathcal{B}_0 \cdot \sum_{i=1}^N \mathbf{m}_{op}(i) \quad (12.37)$$

where  $\mathbf{m}_{op}(i)$  is a magnetic moment operator<sup>20</sup> for the  $i^{th}$  atom and  $\mathcal{H}_0$  is the non-magnetic part of the *hamiltonian*.<sup>21,22</sup> The “magnetization” operator (total magnetic moment per unit volume) is

$$\mathcal{M}_{op} = \frac{1}{V} \sum_{i=1}^N \mathbf{m}_{op}(i). \quad (12.40)$$

<sup>19</sup>An Appendix to the chapter includes a discussion of the implications and limitations of using  $\mathcal{B}_0$  in the thermodynamics.

<sup>20</sup> $\mathbf{m}_{op}$  is proportional to an angular momentum (spin) operator  $\mathcal{S}_{op}$ , with

$$\mathbf{m}_{op} = \frac{g\gamma_B}{\hbar} \mathcal{S}_{op}. \quad (12.38)$$

Here  $g$  is the particle  $g$ -factor and  $\gamma_B = \frac{e\hbar}{2mc}$  is the Bohr magneton (cgs-Gaussian units.)

For a spin 1/2 atom the quantum mechanical  $z$ -component spin operator  $S_z$ , is taken with two eigenstates and two eigenvalues

$$S_z \left| \pm \frac{1}{2} \right\rangle = \pm \frac{\hbar}{2} \left| \pm \frac{1}{2} \right\rangle \quad (12.39)$$

<sup>21</sup>It is assumed that there are no interactions corresponding to internal fields,  $\mathcal{B}_{int}$ .

<sup>22</sup>Field-particle current terms  $\mathcal{H}^{\mathcal{A} \cdot \mathcal{J}} = \frac{1}{2m} \left( p_{op} - \frac{q}{c} \mathcal{A}_{op} \right)^2$ , where  $\mathcal{A}_{op}$  is the vector potential operator, are ignored.

A primary objective is to find the macroscopic Equation of State  $\mathcal{M} = \mathcal{M}(T, \mathcal{B}_0)$  where  $\mathcal{M}$  is the *average* magnetization per unit volume

$$\mathcal{M} = \mathcal{T}r \rho_{op}^\tau \mathcal{M}_{op}. \quad (12.41)$$

### 12.1.3.1 *Simple Paramagnetism*

Consider a spin-1/2 atom which in the absence of a magnetic field has a state with energy  $E_0$ <sup>23</sup> which is two-fold degenerate with magnetic moment eigenstates<sup>24</sup>

$$\mathbf{m}_{\mathbf{z}, \text{op}} |\bar{\mu}_{\pm\frac{1}{2}}\rangle = \pm \frac{g\gamma_B}{2} |\bar{\mu}_{\pm\frac{1}{2}}\rangle. \quad (12.42)$$

In a uniform magnetic field,  $\mathcal{B}_{0,z}$ , the degeneracy of each atom state is lifted, creating a pair of non-degenerate states

$$E_- = E_0 - \mu_{\frac{1}{2}} \mathcal{B}_{0,z} \quad \text{and} \quad E_+ = E_0 + \mu_{\frac{1}{2}} \mathcal{B}_{0,z} \quad (12.43)$$

with  $\mu_{\frac{1}{2}} = \frac{g\gamma_B}{2}$  [See Fig. 12.1].

The macroscopic  $N$ -atom eigen-energies are

$$E(n_+, n_-) = N E_0 + (n_+ - n_-) \mu_{\frac{1}{2}} \mathcal{B}_{0,z} \quad (12.44)$$

where  $n_+$  is the number of atoms with eigen-energy

$$E_+ = E_0 + \mu_{\frac{1}{2}} \mathcal{B}_{0,z} \quad (12.45)$$

and  $n_-$  is the number of atoms with eigen-energy

$$E_- = E_0 - \mu_{\frac{1}{2}} \mathcal{B}_{0,z}, \quad (12.46)$$

with  $n_+ + n_- = N$ .

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<sup>23</sup> $\mathcal{H}_0$  is assumed to make no magnetic contribution, either from interacting moments, internal currents or other internal fields.

<sup>24</sup>For atomic spin  $J$ ,  $\mathbf{m}_{\mathbf{z}, \text{op}}$  defines an eigenvalue equation

$$\mathbf{m}_{\mathbf{z}, \text{op}} |\bar{\mu}_{m_J}\rangle = g\gamma_B m_J |\bar{\mu}_{m_J}\rangle$$

where  $|\bar{\mu}_{m_J}\rangle$  are the eigenstates and  $g\gamma_B m_J$  the eigenvalues, with  $-J \leq m_J \leq J$ .

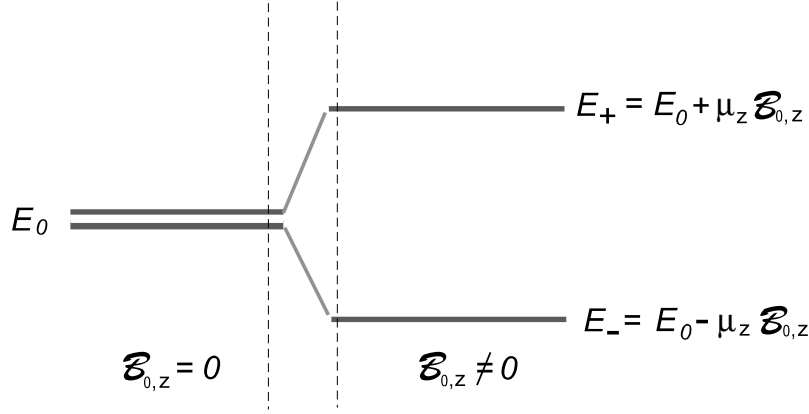


Figure 12.1: Lifting the  $s = 1/2$  spin degeneracy with a magnetic field  $\mathcal{B}_{0,z}$

The probabilities required in the thermodynamic density operator

$$\rho_{op}^T = \sum_s \mathbf{P}(\epsilon_s) |E_s\rangle \langle E_s| \quad (12.47)$$

are found by applying the “least bias” postulate, with a *Lagrangian*

$$\begin{aligned} \mathcal{L} = & -k_B \sum_{n_+, n_- = 0}^N \mathbf{P}(n_+, n_-) \ln \mathbf{P}(n_+, n_-) - \lambda_0 \sum_{n_+, n_- = 0}^N \mathbf{P}(n_+, n_-) \\ & - \lambda_1 \sum_{n_+, n_- = 0}^N \mathbf{P}(n_+, n_-) [NE_0 + \mu_{\frac{1}{2}}(n_+ - n_-) \mathcal{B}_{0,z}] \end{aligned} \quad (12.48)$$

where the  $N$ -atom macroscopic eigen-energies are

$$E = (E_0 - \mu_{\frac{1}{2}} \mathcal{B}_{0,z}) n_- + (E_0 + \mu_{\frac{1}{2}} \mathcal{B}_{0,z}) n_+ \quad (12.49)$$

and  $\lambda_1 = 1/T$ . The resulting probabilities are

$$\mathbf{P}(n_+, n_-) = \frac{e^{-\beta [NE_0 + \mu_{\frac{1}{2}}(n_+ - n_-) \mathcal{B}_{0,z}]}}{\mathcal{Z}_M} \quad (12.50)$$

where  $\beta = 1/k_B T$ , and the denominator (the partition function) is

$$\mathcal{Z}_M = \sum_{\substack{n_+, n_- \\ n_+ + n_- = N}}^N g(n_+, n_-) e^{-\beta [NE_0 + \mu_{\frac{1}{2}}(n_+ - n_-) \mathcal{B}_{0,z}]} \quad (12.51)$$

where the sum is over all states as accounted for by the configurational degeneracy

$$g(n_+, n_-) = \frac{N!}{n_+! n_-!} \quad (12.52)$$

so that

$$\mathcal{Z}_M = \sum_{\substack{n_+, n_- \\ n_+ + n_- = N}} \frac{N!}{n_+! n_-!} e^{-\beta [NE_0 + \mu_{\frac{1}{2}}(n_+ - n_-) \mathcal{B}_{0,z}]} \quad (12.53)$$

which is the binomial expansion of

$$\mathcal{Z}_M = e^{-\beta NE_0} \left( e^{\beta \mu_{\frac{1}{2}} \mathcal{B}_{0,z}} + e^{-\beta \mu_{\frac{1}{2}} \mathcal{B}_{0,z}} \right)^N \quad (12.54)$$

$$= \left[ 2e^{-\beta E_0} \cosh(\beta \mu_{\frac{1}{2}} \mathcal{B}_{0,z}) \right]^N \quad (12.55)$$

### 12.1.3.2 Paramagnet Thermodynamics

Using Eq.12.50 paramagnetic properties can be found.

1. The average *total magnetization* is

$$\langle \mathbf{M} \rangle = - \frac{\sum_{\substack{n_+, n_- \\ n_+ + n_- = N}} \frac{N!}{n_+! n_-!} [\mu_{\frac{1}{2}}(n_+ - n_-)] e^{-\beta [NE_0 + \mu_{\frac{1}{2}}(n_+ - n_-) \mathcal{B}_{0,z}]} }{\mathcal{Z}_M} \quad (12.56)$$

or, equivalently,

$$\langle \mathbf{M} \rangle = - \frac{\partial}{\partial \mathcal{B}_{0,z}} \left( - \frac{1}{\beta} \ln \mathcal{Z}_M \right) \quad (12.57)$$

$$= N \mu_{\frac{1}{2}} \tanh(\beta \mu_{\frac{1}{2}} \mathcal{B}_{0,z}) \quad (12.58)$$

Eq.12.58 is called the Langevin paramagnetic equation. Note in Figure 12.2 that the magnetization attains its maximum value (saturates) as  $\beta \mu_{1/2} \mathcal{B}_0 \rightarrow \infty$ , i.e. where

$$\tanh(\beta \mu_{\frac{1}{2}} \mathcal{B}_{0,z}) \rightarrow 1. \quad (12.59)$$

Therefore the saturation value of  $\langle \mathbf{M} \rangle$  is

$$\langle \mathbf{M} \rangle \approx N \mu_{\frac{1}{2}}. \quad (12.60)$$

The linear region where  $\beta \mu_{\frac{1}{2}} \mathcal{B}_0 \ll 1$  is called the Curie regime. In that case

$$\tanh(\beta \mu_{\frac{1}{2}} \mathcal{B}_{0,z}) \approx \beta \mu_{\frac{1}{2}} \mathcal{B}_{0,z} \quad (12.61)$$

and

$$\langle \mathbf{M} \rangle \approx N \beta \mu_{\frac{1}{2}}^2 \mathcal{B}_{0,z} \quad (12.62)$$

2. The *internal energy* (including the magnetization-dependent energy) is

$$\mathcal{U} = \frac{\sum_{n_+, n_-}^N \frac{N!}{n_+! n_-!} [N E_0 + (n_+ - n_-) \mu_{\frac{1}{2}} \mathcal{B}_{0,z}] e^{-\beta [N E_0 + (n_+ - n_-) \mu_{\frac{1}{2}} \mathcal{B}_{0,z}]} }{\mathcal{Z}_M} \quad (12.63)$$

or equivalently

$$\mathcal{U} = -\frac{\partial}{\partial \beta} \ln \mathcal{Z}_M, \quad (12.64)$$

which is summed to give

$$\mathcal{U} = N E_0 + N \mu_{\frac{1}{2}} \mathcal{B}_{0,z} \tanh(\beta \mu_{\frac{1}{2}} \mathcal{B}_{0,z}). \quad (12.65)$$

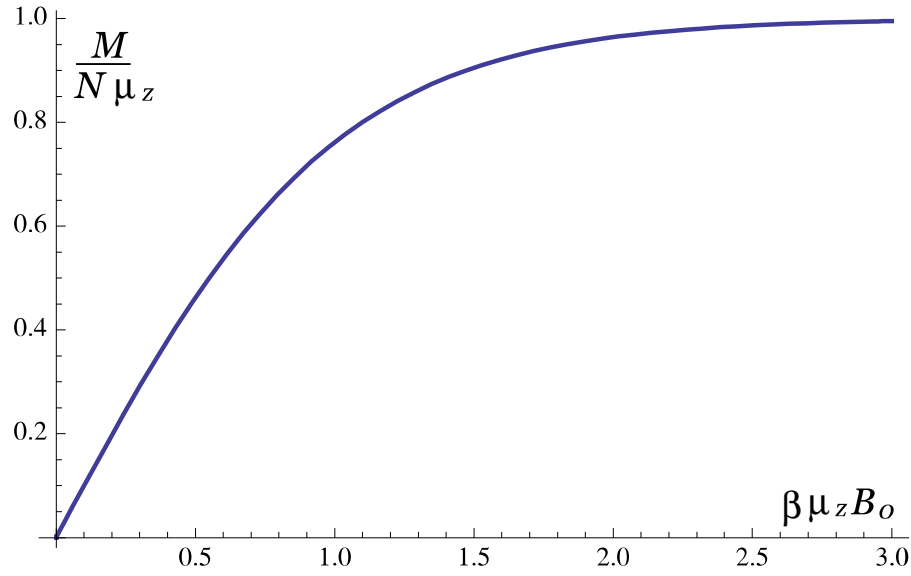
Together with Eq.12.58 and  $\mathcal{U}_0 = N E_0$ , this is equivalent to

$$\mathcal{U} = \mathcal{U}_0 + \langle \mathbf{M} \rangle \mathcal{B}_{0,z}. \quad (12.66)$$

3. Comparing Eq.12.57 with Eq.12.28 we see that the uniform field *Gibbs* potential is found from the uniform field *partition function*, Eq.12.54,

$$G = -\frac{1}{\beta} \ln \mathcal{Z}_M. \quad (12.67)$$

as discussed in Appendix G.

Figure 12.2: Magnetization vs.  $\beta\mu_z B_0$ 

4. From Eq.12.28 the entropy is

$$\mathcal{S} = - \left( \frac{\partial G}{\partial T} \right)_{p, B_0, z} \quad (12.68)$$

$$= k_B \beta^2 \left( \frac{\partial G}{\partial \beta} \right)_{p, B_0, z} \quad (12.69)$$

$$= N k_B \{ \ln 2 + \ln [\cosh(\beta\mu_z B_0)] - \beta\mu_z B_0 \tanh(\beta\mu_z B_0) \} \quad (12.70)$$

The entropy is represented in Figure 12.4. Note that as  $\beta\mu_z B_0 \rightarrow 0$  the entropy attains its maximum value  $\mathcal{S}_{max} = k_B \ln 2$ , reflecting the original 2-fold degeneracy of the atom states.

5. The relevant heat capacities for paramagnets are those for which  $\mathcal{B}$  or  $\mathbf{M}$  are maintained constant. As can be derived from Eq.12.26 the heat capacity at constant  $\mathcal{B}$  is

$$c_{\mathcal{B}} = \left( \frac{\partial H}{\partial T} \right)_{\mathcal{B}} \quad (12.71)$$

or in terms of entropy  $\mathcal{S}$

$$c_{\mathcal{B}} = T \left( \frac{\partial \mathcal{S}}{\partial T} \right)_{\mathcal{B}}. \quad (12.72)$$

Using Eqs.12.70 and 12.72

$$C_B = Nk_B (\beta\mu_{\frac{1}{2}}\mathcal{B}_{0,z})^2 \operatorname{sech}^2(\beta\mu_{\frac{1}{2}}\mathcal{B}_{0,z}) \quad (12.73)$$

a result which is shown in Figure 12.3. For  $\beta\mu_{\frac{1}{2}}\mathcal{B}_0 \ll 1$  this becomes

$$C_B \approx Nk_B (\mu\beta\mathcal{B}_0)^2 . \quad (12.74)$$

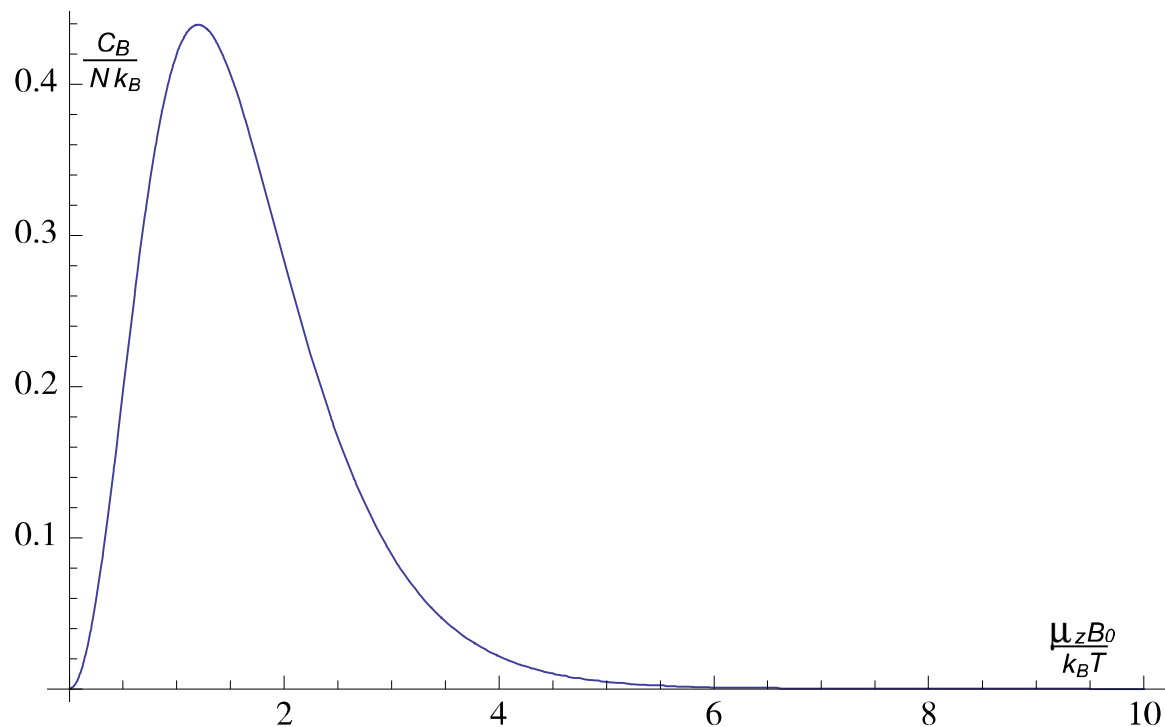


Figure 12.3: Constant field heat capacity  $C_B/Nk_B$  vs.  $\beta\mu_{\frac{1}{2}}\mathcal{B}_0$ .

The heat capacity at constant  $\mathbf{M}$ , as derived from Eq.12.25, is

$$C_M = \left( \frac{\partial \mathcal{U}}{\partial T} \right)_M \quad (12.75)$$

or

$$C_M = T \left( \frac{\partial \mathcal{S}}{\partial T} \right)_M . \quad (12.76)$$

This time Eqs.12.75 and 12.65 are used and obviously give

25

$$C_M = 0 \quad (12.77)$$

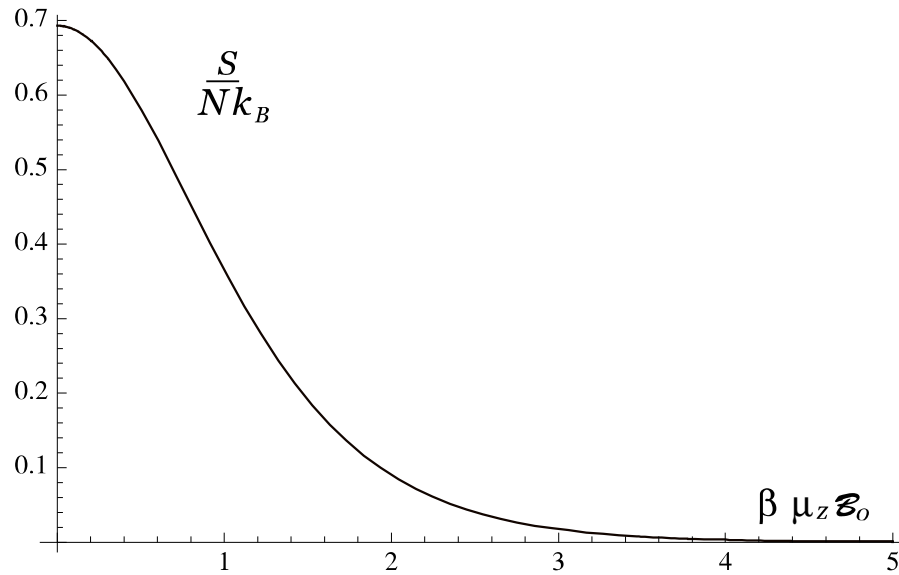


Figure 12.4: Entropy vs.  $\beta \mu_z \mathcal{B}_0$ .

<sup>25</sup>Alternatively, the general relation  $C_M - C_B = T \left( \frac{\partial \mathcal{B}}{\partial T} \right)_M \left( \frac{\partial M}{\partial T} \right)_B$  which can be simplified to  $C_M - C_B = -T \left[ \left( \frac{\partial M}{\partial T} \right)_B \right]^2 \left[ \left( \frac{\partial M}{\partial \mathcal{B}} \right)_T \right]^{-1}$  with its more straightforward partial derivatives, confirms the *zero* result. Derivation of these results is assigned as a problem.



### 12.1.4 Magnetization Fluctuations

State variables *may* exhibit variation about equilibrium average values. These variations are called “fluctuations” and are assigned the symbol  $\Delta$ .<sup>26,27</sup> For example, magnetization “fluctuations”  $\Delta(\mathbf{M})$  are

$$\Delta(\mathbf{M}) \equiv \mathbf{M} - \langle \mathbf{M} \rangle \quad (12.78)$$

and “mean square magnetic fluctuations” (uncertainty) are

$$\langle [\Delta(\mathbf{M})]^2 \rangle = \langle (\mathbf{M} - \langle \mathbf{M} \rangle)^2 \rangle \quad (12.79)$$

$$= \langle \mathbf{M}^2 \rangle - \langle \mathbf{M} \rangle^2 \quad (12.80)$$

where

$$\langle \mathbf{M}^2 \rangle = - \frac{\sum_{n_-, n_+}^N \frac{N!}{n_+! n_-!} [\mu_{\frac{1}{2}}(n_+ - n_-)]^2 e^{-\beta [NE_0 + \mu_{\frac{1}{2}}(n_+ - n_-) \mathcal{B}_{0,z}]} }{\mathcal{Z}_M}. \quad (12.81)$$

Taking this result, together with  $\mathcal{Z}_M$  and  $\langle \mathbf{M} \rangle$  (as calculated in Eq.12.56), the mean square fluctuation is

$$\langle \mathbf{M}^2 \rangle - \langle \mathbf{M} \rangle^2 = \frac{1}{\beta^2} \frac{\partial^2}{\partial \mathcal{B}_0^2} \ln \mathcal{Z}_M \quad (12.82)$$

$$= N \mu_{\frac{1}{2}}^2 \operatorname{sech}^2(\beta \mu_{\frac{1}{2}} \mathcal{B}_0) \quad (12.83)$$

Expressed as dimensionless “root mean square fluctuations”

$$\frac{\sqrt{\langle \mathbf{M}^2 \rangle - \langle \mathbf{M} \rangle^2}}{\langle \mathbf{M} \rangle} = \frac{1}{\sqrt{N} \sinh(\beta \mu_{\frac{1}{2}} \mathcal{B}_{0,z})}, \quad (12.84)$$

which decreases rapidly with increasing field  $\mathcal{B}_0$ , with decreasing temperature  $T$  and with increasing  $N$ .

<sup>26</sup>Generally speaking, vanishingly small fluctuations assure meaningful thermodynamic descriptions.

<sup>27</sup>Fluctuations are associated with thermal state functions that have quantum operator representations. For example, temperature does not have well defined fluctuations since there is no quantum temperature operator. See, e.g. C Kittel, “Temperature Fluctuation: An Oxymoron,” *Physics Today*, **41**(5), 93 (1988).

### 12.1.4.1 Example: Adiabatic (Isentropic) Demagnetization

A paramagnetic needle immersed in liquid  $He^4$  initially at temperature  $T_0$ , is placed in a weak external field  $\mathcal{B}_0$  directed along the needle's long axis.<sup>28</sup> The magnetic field is suddenly lowered to a value  $\mathcal{B}_\ell$ .

What is the change in temperature of the paramagnetic needle? This sudden process corresponds to an adiabatic (*isentropic*) demagnetization – too fast for heat exchange. Therefore, we seek (ignoring irrelevant  $pV$  terms)

$$dT = \left( \frac{\partial T}{\partial \mathcal{B}_0} \right)_S d\mathcal{B}_0 + \left( \frac{\partial T}{\partial \mathcal{S}} \right)_{\mathcal{B}_0} d\mathcal{S} \quad (12.85)$$

which for this isentropic process pares down to

$$dT = \left( \frac{\partial T}{\partial \mathcal{B}_0} \right)_S d\mathcal{B}_0. \quad (12.86)$$

Applying the “cyclic chain rule” [see Chapter 6]

$$\left( \frac{\partial T}{\partial \mathcal{B}_0} \right)_S = - \frac{\left( \frac{\partial \mathcal{S}}{\partial \mathcal{B}_0} \right)_T}{\left( \frac{\partial \mathcal{S}}{\partial T} \right)_{\mathcal{B}_0}} \quad (12.87)$$

$$= - \frac{T}{\mathcal{C}_B} \left( \frac{\partial \mathcal{S}}{\partial \mathcal{B}_0} \right)_T. \quad (12.88)$$

Using the Gibbs potential expression as given in Eq.12.28, and taking cross derivatives we have the Maxwell relation

$$\left( \frac{\partial \mathcal{S}}{\partial \mathcal{B}_0} \right)_T = \left( \frac{\partial \mathbf{M}}{\partial T} \right)_{\mathcal{B}_0} \quad (12.89)$$

so that Eq.12.86 is now

$$dT = - \frac{T}{\mathcal{C}_B} \left( \frac{\partial \mathbf{M}}{\partial T} \right)_{\mathcal{B}_0} d\mathcal{B}_0. \quad (12.90)$$

---

<sup>28</sup>In this configuration the demagnetization factor  $\eta = 0$  which simplifies the situation. [See Section A-5 of the Appendix G.]

Inserting  $\mathcal{C}_{\mathcal{B}}$  from Eq.12.74 and  $\mathbf{M}$  from Eq.12.62 we have

$$\frac{dT}{T} = \frac{d\mathcal{B}_0}{\mathcal{B}_0} \quad (12.91)$$

which is integrated and finally gives

$$T_f = \left( \frac{\mathcal{B}_f}{\mathcal{B}_0} \right) T_0, \quad (12.92)$$

i.e. the needle cools.

### 12.1.5 Weiss Model of Ferromagnetism

In the previous section, paramagnetism is modeled as  $N$  localized moments induced by a magnetic field  $\mathcal{B}_0$  – *the field before matter is inserted*. But moments induced throughout matter are responsible for internal fields which can be modeled as an average *effective* field,  $\mathcal{B}_0 \rightarrow \mathcal{B}^*$ .

Short range, nearest-neighbor magnetic moment coupling is frequently described by the Heisenberg exchange interaction,<sup>29</sup>

$$\mathcal{H}_{ex} = -\frac{1}{2} \mathbf{m}_{op}(i) \mathcal{K}_{i,i'} \mathbf{m}_{op}(i') \quad (12.93)$$

where  $\mathbf{m}_{op}(i)$  is the magnetic moment operator for the  $i^{th}$  site and  $\mathcal{K}_{i,i'}$  is an interaction, which couples the moment at  $i$  and the moment at a nearest neighbor site,  $i'$ . The microscopic hamiltonian,<sup>30</sup> including interactions,<sup>31</sup>

$$\mathcal{H} = -\sum_{i=1}^N \mathcal{B}_0 \cdot \mathbf{m}_{op}(i) - \frac{1}{2} \sum_{i=1}^N \sum_{i'=1}^z \mathbf{m}_{op}(i) \mathcal{K}_{i,i'} \mathbf{m}_{op}(i'), \quad (12.94)$$

where  $z$  is the total number of nearest neighbor moments and the sums include only terms with  $i \neq i'$ .

---

<sup>29</sup>W. Heisenberg, “Mehrkörperproblem und Resonanz in der Quantenmechanik,” Zeitschrift für Physik **38**, 441, (1926).

<sup>30</sup>Curiously, this “magnetic” interaction does not originate from magnetic arguments. Its source is strictly interatomic electronic interactions, in particular from the exchange interaction in the hydrogen molecule.

<sup>31</sup>The factor 1/2 compenstates for the ultimate double counting by the double sum.

Apart from  $1 - D$  or  $2 - D$ , this “many-body” problem has, generally, no analytic solution. But an approximation – a *Mean Field* approximation<sup>32</sup> – can be applied to replace this intractable model by an effective “one-body” problem and plausibly account for the phenomenon of ferromagnetism.

### 12.1.5.1 A Mean Field Approximation – MFA

In preparation for the MFA, rewrite Eq.12.94 as

$$\mathcal{H} = - \sum_{i=1}^N \left\{ \mathcal{B}_0 + \frac{1}{2} \sum_{i'=1}^z \mathcal{K}_{i,i'} \mathbf{m}_{op}(i') \right\} \cdot \mathbf{m}_{op}(i) \quad (12.95)$$

where, assuming an isotropic system, all  $z$  nearest neighbors can be treated as identical, i.e.  $\mathcal{K}_{i,i'} \rightarrow \mathcal{K}$ . Neglecting magnetic moment fluctuations<sup>33</sup>,

$$\Delta(\mathbf{M}) = [\mathbf{m}_{op}(i') - \langle \mathbf{m}_{op} \rangle], \quad (12.97)$$

a “Mean Field Approximation” (MFA) is applied, in which a moment is assumed to interact only with the *average value* of the  $z$  nearest neighbor moments,

$$\mathbf{m}_{op}(i') \rightarrow \langle \mathbf{m}_{op} \rangle \quad (12.98)$$

where  $\mathbf{M} = N \langle \mathbf{m}_{op} \rangle$  is the magnetization. The hamiltonian can then be written in its “mean field” form<sup>34</sup>

$$\mathcal{H} = \frac{1}{2} z N \mathcal{K} \langle \mathbf{m}_{op} \rangle^2 - \sum_{i=1}^N \{ \mathcal{B}_0 + z \langle \mathbf{m}_{op} \rangle \mathcal{K} \} \cdot \mathbf{m}_{op}(i), \quad (12.99)$$

where the leading constant term is from the *MFA*. [See Eq.12.96]. But supplementing the external field  $\mathcal{B}_0$  there is now an “*internal*” field,  $\mathcal{B}_{int}$

$$\mathcal{B}_{int} = \frac{z}{N} \mathbf{M} \mathcal{K} \quad (12.100)$$

---

<sup>32</sup>P Weiss, “L’hypothèse du champ moléculaire et la propriété ferromagnétique.” J. Phys. (Paris) **6**, 661 (1907).

<sup>33</sup>The essence of a mean field approximation is the identity:

$$\begin{aligned} \mathbf{m}_{op}(i') \mathbf{m}_{op}(i) &= [\mathbf{m}_{op}(i') - \langle \mathbf{m}_{op} \rangle] [\mathbf{m}_{op}(i) - \langle \mathbf{m}_{op} \rangle] \\ &\quad + \mathbf{m}_{op}(i') \langle \mathbf{m}_{op} \rangle + \langle \mathbf{m}_{op} \rangle \mathbf{m}_{op}(i) - \langle \mathbf{m}_{op} \rangle \langle \mathbf{m}_{op} \rangle \end{aligned} \quad (12.96)$$

where  $\langle \mathbf{m}_{op} \rangle$  is the average magnetic moment, i.e.  $\mathbf{M}/N$ , the magnetization per site. The MFA neglects the first term, i.e. the product of fluctuations around the magnetization, whereas the last term contributes a constant value.

<sup>34</sup>The double mean field sum over  $i$  and  $i'$  (terms 2 and 3) in Eq.12.96, cancels the factor  $\frac{1}{2}$ .

and a total “effective” field  $\mathcal{B}^*$  at the  $i^{th}$  site

$$\mathcal{B}^*(i) = \mathcal{B}_0(i) + \mathcal{B}_{int}(i) \quad (12.101)$$

$$= \mathcal{B}_0(i) + \frac{z}{N} \mathcal{K} \mathbf{M}(i) \quad (12.102)$$

so that

$$\mathcal{H} = \frac{1}{2} \mathbf{M} \cdot \mathcal{B}_{int} - \sum_{i=1}^N \mathcal{B}^*(i) \cdot \mathbf{m}_{op}(i). \quad (12.103)$$

This has the effect of replacing  $\mathcal{B}_0$  in the paramagnet partition function of Eq.12.55 by  $\mathcal{B}^*$ , in which case

$$\mathcal{Z}_{M^*} = e^{-\frac{1}{2} \beta \mathbf{M} \cdot \mathcal{B}_{int}} [2 \cosh(\beta \mu_{\frac{1}{2}} \mathcal{B}^*)]^N. \quad (12.104)$$

with a Gibbs potential<sup>35</sup>

$$\tilde{G}^* = -\frac{1}{\beta} \ln \mathcal{Z}_{M^*} \quad (12.105)$$

$$= \frac{1}{2} \mathbf{M} \cdot \mathcal{B}_{int} - \frac{N}{\beta} \ln (2 \cosh \beta \mu_{\frac{1}{2}} \mathcal{B}^*). \quad (12.106)$$

In the absence of an external field, i.e.  $\mathcal{B}_0 = 0$ , we find from Eq.12.104

$$\mathbf{M} = N \mu_{\frac{1}{2}} \tanh \left( \beta \mu_{\frac{1}{2}} \frac{z \mathcal{K}}{N} \mathbf{M} \right). \quad (12.107)$$

a transcendental equation in  $\mathbf{M}$ .

### 12.1.5.2 Spontaneous Magnetization – $S=1/2$

Rewriting the  $S = \frac{1}{2}$  result, Eq.12.107, as a self consistent expression in a dimensionless *Order Parameter*  $\mathcal{M}$ ,

$$\mathcal{M} = \frac{\mathbf{M}}{N \mu_{\frac{1}{2}}}, \quad (12.108)$$

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<sup>35</sup>Note the constant term from the *MFA* which has interesting consequences to be discussed in appendix G.[See Eq.12.96.]

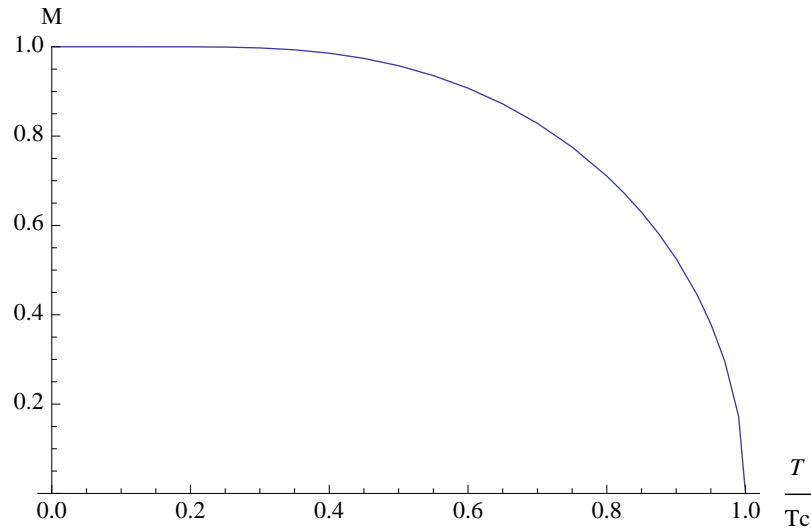


Figure 12.5: A graphical solution of the self-consistent equation, Eq.12.109. The sharp decline of the *Order Parameter*  $\mathcal{M}$  as  $T \rightarrow T_c^-$  (the Curie temperature) is followed by a slope discontinuity at  $T = T_c$ . This is the general characteristic of a magnetic phase transition. When  $T > T_c$  the only solution to Eq.12.109 is  $\mathcal{M} = 0$ .

we have

$$\mathcal{M} = \tanh\left(\frac{T_c}{T}\mathcal{M}\right) \quad (12.109)$$

where

$$T_c = \frac{\mu_{\frac{1}{2}}^2 z \mathcal{K}}{k_B}. \quad (12.110)$$

$T_c$  is called the *Curie temperature*. When  $T < T_c$  magnetic moments spontaneously align within distinct magnetic domains (ferromagnetism). For  $T > T_c$  spontaneous alignment is destroyed, which characterizes  $T_c$  as the “transition temperature” at which a phase transition from an *ordered* ( $\mathcal{M} > 0$ ) to a *disordered* ( $\mathcal{M} = 0$ ) state takes place.<sup>36</sup> [See Figure 12.5.]

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<sup>36</sup>This is usually referred to as *Symmetry Breaking*.

Curie Temperature $K$	
$Fe$	1043
$Co$	1388
$Ni$	627
$Gd$	293
$Dy$	85
$CrBr_3$	37
$EuO$	77
$MnAs$	318
$MnBi$	670
$Fe_2B$	1015
$GdCl_3$	2.2

Table 12.1: F Keffer, Handbuch der Physik, **18**, pt.2, Springer Verlag, New York (1966).

### 12.1.5.3 *Critical Exponents*

As  $T$  approaches  $T_c$  with  $T < T_c$ , the magnetic *order parameter* shows the power-law behavior

$$\mathcal{M} \approx \left( \frac{T_c}{T} - 1 \right)^{\beta_c}, \quad (12.111)$$

where  $\beta_c$  is called a “critical exponent.” The value of  $\beta_c$  from the *MFA* is found by first inverting Eq.12.109

$$\frac{T_c}{T} \mathcal{M} = \tanh^{-1} \mathcal{M} \quad (12.112)$$

and then expanding  $\tanh^{-1} \mathcal{M}$  for small  $\mathcal{M}$

$$\frac{T_c}{T} \mathcal{M} = \mathcal{M} + \frac{1}{3} \mathcal{M}^3 + \dots \quad (12.113)$$

to give

$$\mathcal{M} \approx \sqrt{3} \left( \frac{T_c}{T} - 1 \right)^{1/2}. \quad (12.114)$$

The  $S = \frac{1}{2}$  *MFA* critical exponent is therefore

$$\beta_c = 1/2. \quad (12.115)$$

### 12.1.5.4 Curie-Weiss Magnetic Susceptibility ( $T > T_c$ )

At  $T > T_c$  and with no external field, i.e.  $\mathcal{B}_0 = 0$ , nearest neighbor interactions are no longer sufficient to produce spontaneous magnetization. However, upon introduction of an external field  $\mathcal{B}_0$  induced paramagnetic moments will still contribute internal fields, so that within a MFA a total internal field is again  $\mathcal{B}^*$ , as in Eq.12.102.

But for  $T \gg T_c$  Eq.12.107 can be expanded<sup>37</sup> and solved for  $\langle \mathbf{m} \rangle$  to give

$$\langle \mathbf{m} \rangle = \frac{\mu_{\frac{1}{2}}^2}{k_B} (T - T_c)^{-1} \mathcal{B}_0, \quad (12.116)$$

where  $T_c$  is as defined in Eq.12.110. With the magnetic susceptibility  $\chi_M$  defined as<sup>38</sup>

$$\langle \mathbf{m} \rangle = \chi_M \mathcal{B}_0 \quad (12.117)$$

we have

$$\chi_M = \frac{\mu_{\frac{1}{2}}^2}{k_B} (T - T_c)^{-1} \quad (12.118)$$

which is called the Curie-Weiss Law. When  $T \gg T_c$ ,<sup>39</sup> this is a satisfactory description<sup>40</sup> for magnetic susceptibility. But it fails near  $T \approx T_c$ , where the formula displays a singularity.

### 12.1.6 Closing Comment

The study of magnetic matter remains a vast and varied topic that drives contemporary research, both fundamental and applied. The examples discussed in this chapter (paramagnetism and ferromagnetism) are but introductory samples of the role played by quantum mechanics in understanding macroscopic magnetism.

<sup>37</sup> $\tanh(x) \approx x - \frac{1}{3}x^3$ .

<sup>38</sup>Unlike magnetization, magnetic susceptibility has no strict thermodynamic definition. In the case of non-linear materials an isothermal susceptibility  $\chi_M = \left( \frac{\partial M}{\partial \mathcal{B}_0} \right)_T$  is a more practical definition.

<sup>39</sup> $T_c$  experimentally determined from Curie-Weiss behavior is usually higher than  $T_c$  from the ferromagnetic phase transition.

<sup>40</sup>The Curie-Weiss law is often expressed in terms of  $\frac{1}{\chi_M}$  which is linear in  $T - T_c$ .