Chapter 5
Thermal Properties of Itinerant Magnets

5.1 Difficulties Involved in the Spin Fluctuation Theory of Specific Heat

Temperature dependence of the specific heat of weak itinerant electron ferromagnets in a wide range of temperature was treated by Makoshi and Moriya [1]. The free energy used by them is written by

$$F(M,T) = F_{\rm SW}(M,T) + F_{\rm sf}(M,T,\chi^{-1}(T)). \tag{5.1}$$

It consists of the Stoner-Wohlfarth free energy $F_{\rm SW}$ and the contribution $F_{\rm sf}$ from thermal spin fluctuations. At low temperatures for exchange-enhanced paramagnets, it reduces to that of paramagnon theories for them. Moreover for ferromagnets, it can also be applied to properties at higher temperatures in the paramagnetic phase where the Curie-Weiss law temperature dependence of magnetic susceptibility is observed. Nevertheless, there exist the following difficulties:

1. As shown in the left figure of Fig. 5.1, a curious negative steep decrease of the specific heat appears just above the critical temperature with decreasing temperature.
2. It is based on the free energy that violates rotational invariance in the spin space. This is because only the transverse components of spin fluctuations are included in their treatment. Otherwise, spontaneous magnetic moment shows discontinuous change at the critical temperature.
3. Effects of zero-point spin fluctuations are neglected from the beginning.
4. The effect of the external magnetic field has not been treated by them. Their theory was later simply extended by Takeuchi and Masuda [2] to include the external magnetic field effect. Their numerically estimated changes of specific heat under the presence of magnetic fields of Sc_3In are compared with their experiments in Fig. 5.1.

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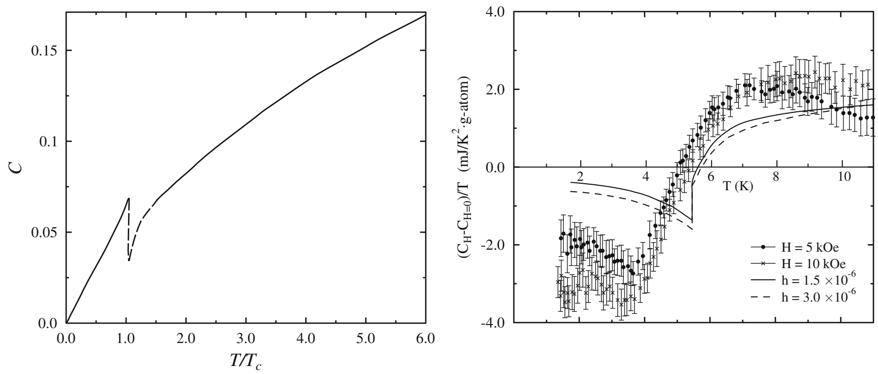

Fig. 5.1 Temperature dependence of the specific heat by Makoshi and Moriya derived from the SCR theory (*left*) and the effect of magnetic field on the specific heat of Sc_3In by Takeuchi and Masuda (*right*)

We will show in the following, how the temperature dependence and the external field effects of entropy and specific heat are derived based on our spin fluctuation theory presented in Chaps. 3 and 4.

5.2 Free Energy of Spin Fluctuations

In order to be consistent with our treatments of various magnetic properties, it will be better for the free energy to satisfy the following requirements:

- It is consistent with the total spin amplitude conservation (TAC). Then, the effect of zero-point spin fluctuations has to be included.
- The rotationally invariant treatment in the spin space has to be made. Thus, both the effects of transverse and the perpendicular components of spin fluctuations have to be included in the free energy.
- As a thermodynamically consistent treatment, the Maxwell relation on the external field effect of the magnetic entropy has to be satisfied.

5.2.1 Free Energy in the Presence of Magnetic Moment

For our treatments of properties in the magnetically ordered phase as well as effects of the external magnetic field, let us assume the following free energy:

$$F(y, \sigma, t) = F_0(y, \sigma, t) + \Delta F(\sigma, t)$$

$$
\begin{aligned}
F_0(y, \sigma, t) = F_{\rm sw} + \frac{2}{\pi}\Bigg[&\sum_q \int_0^{\nu_c} \mathrm{d}\nu\ \frac{\nu}{2}\frac{\Gamma_q}{\Gamma_q^2+\nu^2} \\
&+ \sum_{q_{\rm sw}<q}\int_0^{\infty} \mathrm{d}\nu\ T\ln(1-\mathrm{e}^{-\nu/T})\frac{\Gamma_q}{\Gamma_q^2+\nu^2}\Bigg] \\
+ \frac{1}{\pi}\sum_q \int_0^{\nu_c} \mathrm{d}\nu\ &\left[\frac{\nu}{2} + T\ln(1-\mathrm{e}^{-\nu/T})\right]\frac{\Gamma_q^z}{(\Gamma_q^z)^2+\nu^2} + N_0 T_A y\sigma^2 \\
\Delta F(\sigma, t) = -\frac{1}{3}N_0 T_A &\langle S_{\rm loc}^2\rangle_{\rm tot}[2y+y_z] + \Delta F_1(\sigma, t)
\end{aligned}
\tag{5.2}
$$

Aside from the additional contribution from zero-point spin fluctuations, the term F_0 in the first line corresponds to the free energy of the SCR theory. Both the perpendicular and parallel components of fluctuations with respect to the induced static moment are also included in F_0. The correction of the free energy ΔF, consisting of two contributions, will play significant role to satisfy the spin amplitude conservation, as will be shown in later subsections.

5.2.2 Stability Conditions of the Free Energy

In the following, let us assume that the free energy in (5.2) is a function of independent variables of σ, y, and the reduced temperature t. Since $\Delta y_z(\sigma, t) = y_z(\sigma, t) - y(\sigma, t)$ is regarded as a function of σ and t, it should not be regarded as an independent variable. These parameters are also assumed to be determined by the following conditions:

- From the stability condition of the free energy with respect to the variation of y, i.e., from $\partial F(y, \sigma, t)/\partial y = 0$, the following total spin amplitude conservation is derived.

$$
N_0 T_A\left[\langle \delta S_{\rm loc}^2\rangle_{\rm Z}(y, y_z) + \langle \delta S_{\rm loc}^2\rangle_{\rm T}(y, y_z) + \sigma^2 - \langle S_{\rm loc}^2\rangle_{\rm tot}\right] = 0. \tag{5.3}
$$

The thermal and zero-point components of spin amplitudes are written in the form

$$
\begin{aligned}
\langle S_{\rm loc}^2\rangle_{\rm T}(y, y_z) &= \frac{3T_0}{T_A}[2A(y, t) + A(y_z, t)], \\
\langle S_{\rm loc}^2\rangle_{\rm Z}(y, y_z) &= \langle S_{\rm loc}^2\rangle_{\rm Z}(0, 0) - c\frac{3T_A}{T_0}(2y + y_z).
\end{aligned}
\tag{5.4}
$$

The y dependence of the free energy in (5.2) results mainly from the implicit dependence through that of damping constants Γ_q and Γ_q^z defined in (2.79).

- The thermodynamic relation, $\partial F/\partial M = H$, has to be satisfied. Under the condition where the stability condition $\partial F(y,\sigma,t)/\partial y = 0$ is satisfied, its σ-derivative is given by

$$\frac{\partial F(y,\sigma,t)}{\partial \sigma} = 2N_0 T_A y\sigma + N_0 T_A \left[\langle (S_i^z)^2\rangle(y_z,t) - \frac{1}{3}\langle S_{\rm loc}^2\rangle_{\rm tot}\right]\frac{\partial \Delta y_z}{\partial \sigma} + \frac{\partial \Delta F_1}{\partial \sigma}. \quad (5.5)$$

The first term in the right hand side is equal to the external magnetic field $N_0 h$. The second term results from the Δy_z dependence of the parallel component of the spin fluctuations and the correction ΔF. With using (5.3), it can also be written as follows:

$$\begin{aligned}\langle (S_i^z)^2\rangle(y_z,t) - \frac{1}{3}\langle S_i^2\rangle_{\rm tot} &= \frac{1}{3}\left[2\langle (S_i^z)^2\rangle(y_z,t) - \langle (S_i^\perp)^2\rangle(y,t) - \sigma^2\right] \\ &= \frac{2T_0}{T_A}[A(y_z,t) - A(y,t) - c\Delta y_z] - \frac{1}{3}\sigma^2. \quad (5.6)\end{aligned}$$

For $\sigma = 0$ in the absence of the magnetization, the above right hand side vanishes identically. Then the thermodynamic relation,

$$\frac{\partial F}{\partial \sigma} = 2N_0 T_A y\sigma = N_0 h, \quad (5.7)$$

is satisfied without introducing the correction term ΔF_1 in this case. Whereas for $\sigma \neq 0$, ΔF_1 is necessary, so that the last two terms in (5.5) cancel with each other. The correction ΔF_1 is thus defined by

$$\frac{1}{N_0 T_A}\frac{\partial \Delta F_1}{\partial \sigma} + \lambda(\sigma,t)\frac{\partial \Delta y_z}{\partial \sigma} = 0, \quad (5.8)$$

where $\lambda(\sigma,t)$ as the function of σ and t is also defined by

$$\lambda(\sigma,t) = \frac{2T_0}{T_A}[A(y+\Delta y_z,t) - A(y,t) - c\Delta y_z] - \frac{1}{3}\sigma^2. \quad (5.9)$$

5.2.3 Free Energy Corrections

Before proceeding further, we will show below how the σ dependence of $\Delta F_1(\sigma,t)$ is determined from its definition of (5.8) and (5.9) for $\lambda(\sigma,t)$ in the case of weak external magnetic field.

In the Paramagnetic Phase From the σ dependence of $y(\sigma, t)$ and $y_z(\sigma, t)$ in (3.48), $\Delta y_z(\sigma, t)$ is given by

$$\Delta y_z(\sigma, t) = 2y_1(t)\sigma^2 + \cdots . \tag{5.10}$$

By substituting the above result for (5.9), we obtain the σ dependence of $\lambda(\sigma, t)$ given by

$$\lambda(\sigma, t) = -\frac{4}{15}\left[1 - \frac{1}{c}A'(y, t)\right]\frac{y_1(t)}{y_1(0)}\sigma^2 - \frac{1}{3}\sigma^2 + \cdots = -\frac{3}{5}\sigma^2 + \cdots , \tag{5.11}$$

with use of the relations $T_A/T_0 = 15cy_1(0)$ in (3.10), and $y_1(t) = y_1(0)/[1 - A'(y, t)/c]$ in (3.50). By putting these results into (5.8), the correction $\Delta F_1(\sigma, t)$ is evaluated as follows:

$$\frac{1}{N_0 T_A}\Delta F_1(\sigma, t) = -4y_1(t)\int_0^{\sigma} \sigma'\lambda(\sigma', t)\mathrm{d}\sigma' = \frac{3}{5}y_1(t)\sigma^4 + \cdots . \tag{5.12}$$

In the Magnetically Ordered Phase If we notice the σ dependence of $y(\sigma, t)$ and $y_z(\sigma, t)$ in (4.2), $\Delta y_z(\sigma, t)$ is given by

$$\Delta y_z(\sigma, t) = 2y_1(t)\sigma^2 = 2y_1(t)\sigma_0^2(t) + 2y(\sigma, t).$$

As with the derivation of (5.11), the substitution of the above result for (5.9) gives the following expression of $\lambda(\sigma, t)$:

$$\begin{aligned}
\lambda(\sigma, t) &= \lambda(\sigma_0, t) + \delta\lambda(\sigma, t) \\
\lambda(\sigma_0, t) &= -\left[\frac{1}{3} + \frac{4y_1(t)}{15y_1(0)}\right]\sigma_0^2(t) + \frac{2}{15cy_1(0)}\left[A(2y_1\sigma_0^2, t) - A(0, t)\right] \\
\delta\lambda(\sigma, t) &= -\left\{\frac{1}{3} + \frac{4y_1(t)}{15y_1(0)}\left[1 - \frac{3}{2c}A'(2y_1\sigma_0^2, t) + \frac{1}{2c}A'(0, t)\right]\right\} \\
&\quad \times[\sigma^2 - \sigma_0^2(t)] + \cdots
\end{aligned} \tag{5.13}$$

The first term $\lambda(\sigma_0, t)$ represents the effect of the appearance of $\sigma_0(t)$, while the second term $\delta\lambda(\delta, t)$ is induced by external magnetic field. In the limit of zero-temperature, they reduce to

$$\lambda(\sigma_0, 0) = -\frac{3}{5}\sigma_0^2(0), \quad \delta\lambda(\sigma, 0) = -\frac{3}{5}[\sigma^2 - \sigma_0^2(0)]. \tag{5.14}$$

The correction $\Delta F_1(\sigma, t)$ is then evaluated by the following integration of (5.8) with respect to σ.

$$\frac{1}{N_0 T_A}\Delta F_1(\sigma, t) = -\int [\lambda(\sigma_0, t) + \delta\lambda(\sigma', t)]\frac{\partial \Delta y_z}{\partial \sigma'}\mathrm{d}\sigma'$$

$$= -\lambda(\sigma_0, t) \int \mathrm{d}\Delta y_z - 4y_1(t) \int \sigma' \delta\lambda(\sigma', t) \mathrm{d}\sigma', \tag{5.15}$$

where the approximation, $\partial \Delta y_z / \partial \sigma \simeq 4y_1(t)\sigma$, is used in the last line. The result is written in the form,

$$\begin{aligned} \frac{1}{N_0 T_A} \Delta F_1(\sigma, t) &= -\lambda(\sigma_0, t) \Delta y_z(\sigma, t) \\ &+ y_1(t) \left\{ \frac{1}{3} + \frac{4y_1(t)}{15y_1(0)} \left[1 - \frac{3}{2c} A'(2y_1\sigma_0^2, t) + \frac{1}{2c} A'(0, t) \right] \right\} \\ &\times [\sigma^2 - \sigma_0^2(t)]^2. \end{aligned} \tag{5.16}$$

Note the presence of the first correction term even in the absence of the external magnetic field. In the limit $\sigma_0(t) = 0$, it agrees with (5.12) in the paramagnetic phase.

At the Critical Temperature In this case, substitution of the $\sqrt{y}$ linear dependence for the thermal amplitude in (5.9) leads to the following expression:

$$\begin{aligned} \lambda(\sigma, t_c) &\simeq -\frac{2T_0}{T_A} \frac{\pi t_c}{4} (\sqrt{y_z} - \sqrt{y}) - \frac{1}{3}\sigma^2 = -\left[\frac{\pi T_c}{2T_A} \sqrt{y_c} (\sqrt{5} - 1) + \frac{1}{3} \right] \sigma^2 \\ &= -\frac{\sqrt{5}}{\sqrt{5} + 2} \sigma^2, \end{aligned} \tag{5.17}$$

with using the critical magnetic isotherms $y(\sigma, t_c) = y_c\sigma^4$ and $y_z(\sigma, t_c) = 5y_c\sigma^4$. The critical free energy correction is therefore given by

$$\Delta F_1(\sigma, t_c) \simeq -16 N_0 T_A y_c \int_0^\sigma \sigma'^3 \lambda(\sigma', t_c) \mathrm{d}\sigma' = N_0 T_A \frac{8\sqrt{5} y_c}{3(2 + \sqrt{5})} \sigma^6. \tag{5.18}$$

The coefficient $y_1(t)$ of the σ^4 term of the free energy vanishes at the critical point. The correction ΔF_1 also becomes proportional to σ^6.

We have shown that the free energy in (5.2) is consistent with the TAC condition. The variational condition of the free energy with respect to the variable y agrees with the TAC condition. In the case of systems with the finite induced magnetization σ, we need to introduce the extra correction term $\Delta F_1(\sigma, t)$ in the free energy. Otherwise the thermodynamic relation is violated.

5.3 Temperature Dependence of Entropy and Specific Heat

In this section, the magnetic entropy is derived from the derivative of the free energy in (5.2) with respect to temperature T. The temperature dependence of the specific heat is then derived by differentiating the entropy again with respect to T.

5.3.1 Temperature Dependence of Paramagnetic Entropy

In the paramagnetic phase, the effect of spin waves, the difference between y and y_z, and the free energy correction ΔF_1 are all neglected in (5.2). Under the condition that $\partial F(y,t)/\partial y = 0$ is satisfied, the entropy is evaluated by differentiating the free energy with respect to temperature.

$$
\begin{aligned}
S_m(y,t) = &-\frac{\partial F(y,t)}{\partial T} = \frac{3}{\pi}\sum_q \left[-\int_0^\infty d\nu \log(1-e^{-\nu/T}) \frac{\Gamma_q}{\nu^2+\Gamma_q^2} \right. \\
&\left. + \frac{1}{T}\int_0^\infty d\nu \frac{1}{e^{\nu/T}-1}\frac{\Gamma_q \nu}{\nu^2+\Gamma_q^2} \right] \\
&= 6\sum_q \left[-\frac{1}{2\pi}\int_0^\infty ds \log(1-e^{-2\pi s}) \frac{u}{s^2+u^2} \right. \\
&\left. + u\int_0^\infty ds \frac{s}{e^{2\pi s}-1}\frac{1}{s^2+u^2} \right],
\end{aligned} \tag{5.19}
$$

where new variables $s = \nu/2\pi T$ and $u(q) = \Gamma_q/2\pi T$ are introduced. In more simplified form, it is also written by

$$
\begin{aligned}
\frac{1}{N_0}S_m(y,t) &= -\frac{1}{N_0 T_0}\frac{\partial F(y,t)}{\partial t}, \\
&= -9\int_0^1 dx x^2[\Phi(u) - u\Phi'(u)], \quad u = x(y+x^2)/t,
\end{aligned} \tag{5.20}
$$

by introducing the new function $\Phi(z)$. A brief explanation of this function is given below.

Integral expression of $\Phi(z)$ The function $\Phi(z)$ is related to the logarithm of the gamma function $\Gamma(z)$ and is expressed in the following integral form:

$$
\begin{aligned}
\Phi(z) &= \log\sqrt{2\pi} - z + \left(z - \frac{1}{2}\right)\ln z - \log\Gamma(z) \\
&= \frac{1}{\pi}\int_0^\infty ds \log(1-e^{-2\pi s})\frac{z}{s^2+z^2}
\end{aligned} \tag{5.21}
$$

The derivative of $\Phi(z)$ by z is equivalent with the integral expression of the digamma function $\psi(z)$.

$$
\begin{aligned}
\Phi'(z) &= \frac{1}{\pi}\int_0^\infty dt \log(1-e^{-2\pi t})\frac{\partial}{\partial z}\left(\frac{z}{t^2+z^2}\right) \\
&= -\frac{1}{\pi}\int_0^\infty dt \log(1-e^{-2\pi t})\frac{\partial}{\partial t}\left(\frac{t}{t^2+z^2}\right)
\end{aligned}
$$

$$= \int_0^\infty dt \frac{2}{e^{2\pi t}-1} \frac{t}{t^2+z^2} = \log z - \frac{1}{2z} - \psi(z)$$

From our expression of the entropy (5.20), the following interesting consequences are derived:

- The following term in the theory of Makoshi and Moriya is absent in (5.20).

$$-\frac{T_A}{T_0}\langle S_{\rm loc}^2\rangle_{\rm T}(t)\frac{dy}{dt} \tag{5.22}$$

  The reason is because it disappears from the stability condition (5.3) of the free energy with respect to y. For the same reason, the effect of zero-point fluctuations does not appear.
- If the above term is present in the entropy, its temperature derivative gives the term proportional to d^2y/dt^2, resulting in the negative peak in the temperature dependence of the specific heat just above the critical point.

5.3.2 Temperature Dependence of the Specific Heat

The paramagnetic specific heat is derived by the temperature derivative of the entropy in (5.20). It is given by

$$\begin{aligned}\frac{1}{N_0 t}C_m(y,t) &= \frac{1}{N_0 T_0}\frac{\partial S(y,t)}{\partial t} = 9\int_0^1 dx x^2\left(-\frac{u}{t}+\frac{x}{t}\frac{dy}{dt}\right)u\Phi''(u)\\ &= -\frac{9}{t}\int_0^1 dx x^2 u^2\Phi''(u) - 9\frac{\partial A(y,t)}{\partial t}\frac{dy}{dt}, \quad u = x(y+x^2)/t\end{aligned} \tag{5.23}$$

The coefficient of the second dy/dt linear term is derived as follows.

If we notice the definition of the thermal amplitude $A(y,t)$ in (2.83), it can also be written in the form

$$A(y,t) = \int_0^1 dx x^3\Phi'(u). \tag{5.24}$$

Under the constant y condition, the partial t derivative of (5.24) is given by

$$-\frac{\partial A(y,t)}{\partial t} = -\frac{\partial}{\partial t}\int_0^1 dx x^3\Phi'(u) = \frac{1}{t}\int_0^1 dx x^3 u\Phi''(u), \tag{5.25}$$

with use of the relation $\partial u/\partial t = -u/t$. Both the integrands, u linear term in (5.23) and the other one in (5.25), are in agreement with each other.

In the Low Temperature Limit In this range of temperature, both the inverse of the magnetic susceptibility $y(t)$ and the thermal amplitude are proportional to t^2. Since their t derivatives are both proportional to t, the second term of (5.23) is proportional to t^2 and is therefore negligible. Main contribution results from the following integral:

$$I(y,t) = -\frac{1}{t}\int_0^1 x^2u^2\Phi''(u)\mathrm{d}x, \quad \Phi''(u) = \left[\frac{1}{u} + \frac{1}{2u^2} - \psi'(u)\right] \tag{5.26}$$

Reflecting to the property of the digamma function, the integrand of (5.26) is approximated by

$$-\frac{1}{t}x^2u^2\Phi''(u) \sim \begin{cases} \dfrac{1}{2t}x^2, & \text{for } u \ll 1 \\ \dfrac{1}{6tu}x^2 = \dfrac{x}{6(y+x^2)}, & \text{for } u \gg 1 \end{cases} \tag{5.27}$$

To find the temperature dependence of the function $I(y,t)$, let us introduce the new variable $x' = x/t^{1/3}$ and represent u by

$$u = x'(y/t^{2/3} + x'^2) = x'(x_0^2 + x'^2), \quad x_0 \equiv y^{1/2}/t^{1/3}.$$

Then only the single parameter x_0 is involved in the integrand. The range of the integration is modified to be $0 \le x' \le 1/t^{1/3}$. Depending on the relative magnitude of x_0 and 1, the integral is estimated as follows:

1. In the case where $x_0 \lesssim 1$ ($y \lesssim t^{2/3}$) is satisfied
   In the range, $x_0 \le x' \le 1/t^{1/3}$, u is approximated by $u \simeq x'^3 = x^3/t$. The integration over the range, $1 \le x' \le 1/t^{1/3}$ within this region, gives

$$I(y,t) \simeq \frac{1}{6}\int_{t^{1/3}}^1 \frac{1}{x}\mathrm{d}x = \frac{1}{12}\log(1/t^{2/3}). \tag{5.28}$$

   Integration from the other region only gives a finite result.
2. In the case, $1 \lesssim x_0$ ($t^{2/3} \lesssim y$).
   The asymptotic expansion in this case is justified for $u \sim x_0^2x' = yx/t > 1$, for $u \sim x_0^2x'$ is satisfied around $x' = 0$. In terms of the original variable x, the integral in this region is evaluated by

$$I(y,t) \simeq \frac{1}{6}\int_{t/y}^1 \frac{x}{y+x^2}\mathrm{d}x = \frac{1}{12}\log\left(\frac{1+y}{y+t^2/y^2}\right) \simeq \frac{1}{12}\log(1/y), \tag{5.29}$$

   where $t^2/y^3 \ll 1$ (i.e., $t^{2/3} \ll y$) is assumed to be satisfied. The integral over the small range $0 \le x \le t/y$ around the origin is also negligible in this case.

To summarize, for exchange-enhanced paramagnets where $y \ll 1$ is satisfied, their temperature dependence of the specific heat at low temperatures is given by

$$\frac{1}{N_0 t}C_m \simeq \begin{cases} \dfrac{1}{2}\log(1/t), & (y \ll t^{2/3}, \text{ or } y/t^{2/3} \ll 1) \\ \dfrac{3}{4}\log(1/y). & (t^{2/3} \ll y, \text{ or } y/t^{2/3} \gg 1). \end{cases} \tag{5.30}$$

These are regarded as characteristic behaviors in the critical region for $z = y/t^{2/3} \ll 1$ in (3.65), and in the low temperature region for $z = y/t^{2/3} \gg 1$ around the QCP.

Temperature Dependence Around the Critical Temperature Around the critical temperature in the paramagnetic phase, we need to deal with the limit $y \to 0$ at finite temperature. In this case, the second term in (5.23) plays a predominant role on the temperature dependence of specific heat as will be shown below.

To begin with, the derivative of (3.30) with respect to temperature t is given as

$$[A'(y,t) - c]\frac{\mathrm{d}y(t)}{\mathrm{d}t} + \frac{\partial A(y,t)}{\partial t} = 0. \tag{5.31}$$

If we note (3.50) for $y_1(t)$ in Chap. 3, (5.31) is also written in the form

$$\frac{\mathrm{d}y(t)}{\mathrm{d}t} = \frac{1}{c - A'(y,t)}\frac{\partial A(y,t)}{\partial t} = \frac{y_1(t)}{c y_1(0)}\frac{\partial A(y,t)}{\partial t}. \tag{5.32}$$

The second term in (5.23) can be therefore given in the form

$$\frac{\partial A(y,t)}{\partial t}\frac{\mathrm{d}y(t)}{\mathrm{d}t} = c\frac{y_1(0)}{y_1(t)}\left[\frac{\mathrm{d}y(t)}{\mathrm{d}t}\right]^2 \simeq \frac{\pi t_c}{8\sqrt{y(t)}}\left[\frac{\mathrm{d}y(t)}{\mathrm{d}t}\right]^2,$$

with using $y_1(t) \propto \sqrt{y(t)}$ in (3.51). Substitution of the dependence of $y(t)$, proportional to $(t - t_c)^2$, for the above expression finally leads to the following dependence:

$$\frac{\partial A(y,t)}{\partial t}\frac{\mathrm{d}y(t)}{\mathrm{d}t} = \frac{\pi t_c}{4\sqrt{2}}(y_c'')^{3/2}(t - t_c), \quad y_c'' = \left.\frac{\mathrm{d}^2 y(t)}{\mathrm{d}t^2}\right|_{t=t_c} = 2\left[\frac{16A(0,t_c)}{3\pi t_c^2}\right]^2,$$

where (3.38) is used to evaluate the second derivative y_c''. The temperature dependence of the specific heat is thus given by

$$\frac{1}{N_0 t}C_m \simeq \frac{1}{2}\log(1/t_c) - \frac{9\pi t_c}{4\sqrt{2}}(y_c'')^{3/2}(t - t_c). \tag{5.33}$$

It increases proportional to $(T_c - T)$ with decreasing temperature toward T_c. For $t_c \ll 1$, since $A(0,t_c) \propto t_c^{4/3}$ is satisfied, the above $(y_c'')^{3/2}$ is proportional to $1/t_c^2$. Then, $[C_m(T) - C_m(T_c)] \propto (T_c - T)/T_0$ is satisfied with a numerical proportional constant.

5.3.3 Temperature Dependence of the Entropy and the Specific Heat in the Ordered Phase

Temperature dependence of the entropy and the specific heat in the magnetically ordered phase is treated in this section. As with the paramagnetic phase, they are given by differentiating the free energy in (5.2) with respect to temperature. Unlike the paramagnetic phase, the correction ΔF_1 of the free energy is necessary.

Temperature Dependence of the Entropy The entropy is derived from the partial temperature derivative of the free energy as given by

$$S_m(\sigma, t) = S_{m0}(\sigma, t) + \Delta S_m(\sigma, t)$$
$$\frac{1}{N_0} S_{m0}(\sigma, t) = -6 \int_{x_c}^{1} \mathrm{d}x x^2 [\Phi(u) - u\Phi'(u)] - 3 \int_0^1 \mathrm{d}x x^2 [\Phi(u_z) - u\Phi'(u_z)] \tag{5.34}$$
$$u = x(y + x^2)/t, \quad u_z = x(y_z + x^2)/t.$$

It consists of two contributions, S_{m0} corresponding to (5.21) in the paramagnetic phase and $\Delta S_m(\sigma, t)$ resulting from the t-dependence of $\Delta y_z(\sigma, t)$ and $\Delta F_1(\sigma, t)$. The effect of spin waves is neglected for simplicity. In the same way as (5.4) for the σ derivative of the free energy, the second term is evaluated by the partial t-derivative of $\Delta y_z(\sigma, t)$ and $\Delta F_1(\sigma, t)$ as given below.

$$\begin{aligned} T_0 \Delta S_m &= -N_0 T_A \left[\langle (S_i^z)^2 \rangle (y_z, t) - \frac{1}{3} \langle S_i^2 \rangle_{\text{tot}} \right] \frac{\partial \Delta y_z}{\partial t} - \frac{\partial \Delta F_1}{\partial t} \\ &= -N_0 T_A \lambda(\sigma, t) \frac{\partial \Delta y_z}{\partial t} - \frac{\partial \Delta F_1}{\partial t}. \end{aligned} \tag{5.35}$$

In the region of weak external magnetic field, the correction ΔF_1 in (5.16) can be approximated by

$$\Delta F_1(\sigma, t) \simeq -N_0 T_A \lambda(\sigma_0, t) \Delta y_z(\sigma, t). \tag{5.36}$$

Substitution of (5.36) for ΔF_1 in (5.35) gives the entropy correction given by

$$\begin{aligned} \Delta S_m(\sigma, t) &= -N_0 \frac{T_A}{T_0} \lambda(\sigma, t) \frac{\partial \Delta y_z}{\partial t} + N_0 \frac{T_A}{T_0} \frac{\partial}{\partial t} [\lambda(\sigma_0, t) \Delta y_z(\sigma, t)] \\ &= N_0 \frac{T_A}{T_0} \left[\frac{\mathrm{d}\lambda(\sigma_0, t)}{\mathrm{d}t} \Delta y_z(\sigma, t) - \delta\lambda(\sigma, t) \frac{\partial \Delta y_z(\sigma, t)}{\partial t} \right], \end{aligned} \tag{5.37}$$

where $\delta\lambda(\sigma, t) = \lambda(\sigma, t) - \lambda(\sigma_0, t)$. The second term proportional to $\delta\lambda(\sigma, t)$ in the second line is neglected in the absence of external magnetic field, since $\delta\lambda(\sigma, t) = 0$ is satisfied for $\sigma = \sigma_0$. The parameter $\lambda(\sigma_0, t)$ defined in (5.9) and its t-derivative are given by

$$\begin{aligned}\lambda(\sigma_0,t) &= \frac{2T_0}{T_A}[A(y_{z0},t)-A(y,t)-cy_{z0}(t)]-5cy_1(0)\sigma_0^2(t)\\ \frac{T_A}{T_0}\frac{\mathrm{d}\lambda(\sigma_0,t)}{\mathrm{d}t} &= 2[A'(y_{z0},t)-c]\frac{\mathrm{d}y_{z0}(t)}{\mathrm{d}t}+2\frac{\partial A(y_{z0},t)}{\partial t}\\ &\quad -5cy_1(0)\frac{\mathrm{d}\sigma_0^2(t)}{\mathrm{d}t}-2\frac{\partial A(0,t)}{\partial t}\end{aligned} \tag{5.38}$$

With the use of the TAC condition, the above t-derivative can be written in two different forms. Notice the t-derivative of the condition (3.3) is given by

$$\frac{\partial A(y_{z0},t)}{\partial t}+[A'(y_{z0},t)-c]\,\frac{\mathrm{d}y_{z0}}{\mathrm{d}t}+2\frac{\partial A(0,t)}{\partial t}+5cy_1(0)\frac{\mathrm{d}\sigma_0^2(t)}{\mathrm{d}t}=0. \tag{5.39}$$

Then $\mathrm{d}\lambda/\mathrm{d}t$ in (5.38) is written in the form

$$\frac{T_A}{T_0}\frac{\mathrm{d}\lambda(\sigma_0,t)}{\mathrm{d}t}=\begin{cases}-6\dfrac{\partial A(0,t)}{\partial t}-15cy_1(0)\dfrac{\mathrm{d}\sigma_0^2(t)}{\mathrm{d}t}, & \text{(I)}\\ 3\dfrac{\partial A(y_{z0},t)}{\partial t}+3[A'(y_{z0},t)-c]\dfrac{\mathrm{d}y_{z0}(t)}{\mathrm{d}t}, & \text{(II)}\end{cases} \tag{5.40}$$

depending on either the terms related to $y_{z0}(t)$ or $\sigma_0^2(t)$ are eliminated. The entropy correction is also expressed in two alternative forms:

$$\frac{1}{N_0}\Delta S_m(t)=\begin{cases}-3y_{z0}(t)\left[2\dfrac{\partial A(0,t)}{\partial t}+5cy_1(0)\dfrac{\mathrm{d}\sigma_0^2(t)}{\mathrm{d}t}\right], & \text{(I)}\\ 3y_{z0}(t)\left\{\dfrac{\partial A(y_{z0},t)}{\partial t}+[A'(y_{z0},t)-c]\dfrac{\mathrm{d}y_{z0}(t)}{\mathrm{d}t}\right\}. & \text{(II)}\end{cases} \tag{5.41}$$

Temperature Dependence of the Specific Heat In the ordered phase, the specific heat is given by the sum of the temperature derivatives of S_{m0} and ΔS_m.

$$\begin{aligned}C_m(t) &= C_{m0}(t)+\Delta C_m(t)\\ \frac{1}{N_0 t}C_{m0}(t) &= 6I_c(0,t)+3I(y_{z0},t), \quad I_c(y,t)=-\frac{1}{t}\int_{x_c}^{1}\mathrm{d}x x^2u^2\Phi''(u)\\ \frac{1}{N_0 t}\Delta C_m(t) &= -3\frac{\partial A(y_{z0},t)}{\partial t}\frac{\mathrm{d}y_{z0}(t)}{\mathrm{d}t}+\frac{1}{N_0}\frac{\mathrm{d}\Delta S_m(t)}{\mathrm{d}t}\\ &= 3y_{z0}(t)\left[\frac{\partial^2 A(y_{z0},t)}{\partial t^2}+A''(y_{z0},t)\left(\frac{\mathrm{d}y_{z0}}{\mathrm{d}t}\right)^2\right.\\ &\qquad\left.+2\frac{\partial A'(y_{z0},t)}{\partial t}\frac{\mathrm{d}y_{z0}(t)}{\mathrm{d}t}\right]\\ &\quad +3[A'(y_{z0},t)-c]\left[\left(\frac{\mathrm{d}y_{z0}(t)}{\mathrm{d}t}\right)^2+y_{z0}(t)\frac{\mathrm{d}^2y_{z0}(t)}{\mathrm{d}t^2}\right]\end{aligned} \tag{5.42}$$

The first term $C_{m0}(t)$ results from the direct t derivative of $S_{m0}(t)$. The function $I(y_{z0}, t)$ in the second line is already defined in (5.26). The correction $\Delta C_m(t)$ consists of the sum of two contributions, i.e., the implicit temperature dependence through that of $y_{z0}(t)$ included in $S_{m0}(t)$ and the t derivative of the correction $\Delta S_m(t)$. It is derived by using the expression (II) in (5.41). If (I) is used, $\Delta C_m(t)$ is written in the form

$$\frac{1}{N_0 t}\Delta C_m(t) = -3\Bigg[\left(2\frac{\partial A(0,t)}{\partial t} + \frac{\partial A(y_{z0},t)}{\partial t}\right)\frac{\mathrm{d}y_{z0}(t)}{\mathrm{d}t} + 2y_{z0}(t)\frac{\partial^2 A(0,t)}{\partial t^2} + 5cy_1(0)\frac{\mathrm{d}}{\mathrm{d}t}\left(y_{z0}(t)\frac{\mathrm{d}\sigma_0^2(t)}{\mathrm{d}t}\right)\Bigg] \quad (5.43)$$

The temperature dependence of $C_m(t)$ shows the following two characteristic features derived from the presence of $\Delta C_m(t)$.

- There exits another new enhancement in the T-linear coefficient of the specific heat in the limit of low temperature.
- A sharp peak appears at the critical temperature.

Numerically calculated results of (5.42) are shown in Fig. 5.2.

Dependence in the Limit of Low Temperature In the limit where $t^{3/2} \ll y_{z0}(t)$ is satisfied, $I(y_{z0}, t)$ is given by (5.29). The transverse contribution $I_c(0, t)$ is of the same size because of the presence of lower cut-off of the integral x_c. The T-linear coefficient of C_{m0} shows the logarithmic behavior:

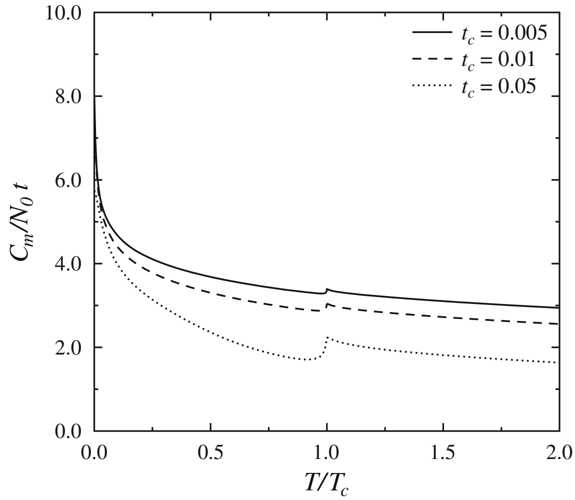

Fig. 5.2 Numerically calculated examples of the temperature dependence of the specific heat for $t_c = 0.005, 0.01, 0.05$ from the top

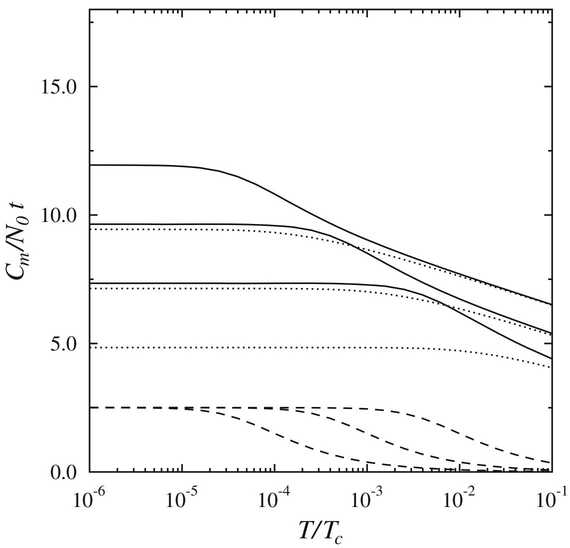

Fig. 5.3 Temperature dependence of the specific heat in the low-T limit for $t_c = 0.0001, 0.001, 0.01$ from the top in logarithmic temperature scale. The dependence of C_m, C_{m0}, and ΔC_m is denoted by *solid*, *dotted*, and *dashed curves*, respectively

$$\frac{1}{N_0 t} C_{m0} \simeq \frac{1}{4}\left[2\log(1/x_c^2) + \log(1/y_{z0})\right] \simeq \frac{3}{2}\log[1/\sigma_0(0)], \tag{5.44}$$

as the spontaneous moment tends to disappear, $\sigma_0(t) \to 0$. Another contribution of considerable size also results from ΔC_m, as given by

$$\begin{aligned}\frac{1}{N_0 t}\Delta C_m &\simeq -3cy_{z0}(t)\frac{\mathrm{d}^2 y_{z0}(t)}{\mathrm{d}t^2} + 3y_{z0}\frac{\partial^2 A(y_{z0}, t)}{\partial t^2} \\ &= \frac{1}{6}\left[\left(\frac{\pi}{4}\right)^4 + 2\left(\frac{\pi}{4}\right)^2 + 4\right].\end{aligned} \tag{5.45}$$

Though it is not divergent in the limit $\sigma_0(t) \to 0$, its size is nonnegligible in the limit of low temperature. The temperature dependence of these two contributions is shown in Fig. 5.3.

Dependence Around the Critical Temperature Around the critical temperature, the opposite condition $y \ll t^{3/2}$ is satisfied for $I(y_{z0}, t)$ in (5.42). The first term $C_{m0}(t)$ is then given by

$$\frac{1}{N_0 t} C_{m0}(t) \simeq 9I(0, t) \simeq \frac{1}{2}\log(1/t). \tag{5.46}$$

As with the case of the paramagnetic phase, the correction ΔC_m shows the $(t - t_c)$-linear dependence from the following dominant contributions:

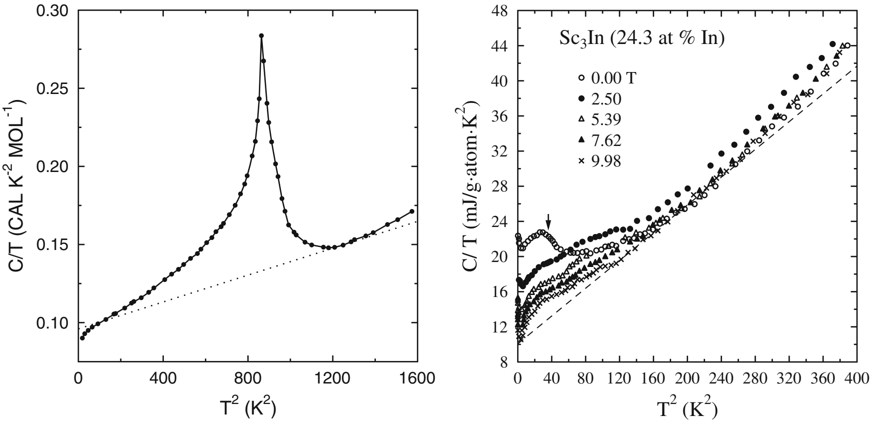

Fig. 5.4 Temperature dependence of the specific heat of MnSi by Fawcett et al. (*left*) and Sc_3In by Ikeda and Gschneidner (*right*)

$$\frac{1}{N_0 t}\Delta C_m(t) \simeq 3\left(\frac{\mathrm{d}y_{z0}(t)}{\mathrm{d}t}\right)^2 \left[y_{z0}(t)A''(y_{z0},t) + 3A'(y_{z0},t)\right] + 3y_{z0}(t)A'(y_{z0},t)\frac{\mathrm{d}^2 y_{z0}(t)}{\mathrm{d}t^2}. \tag{5.47}$$

With the use of the dependence $y_{z0}(t) \propto (t_c - t)^2$ and the critical $\sqrt{y_{z0}}$ dependence of the thermal amplitude $A(y_{z0}, t)$, the above right hand side is estimated as follows:

$$\left(\frac{\mathrm{d}y_{z0}(t)}{\mathrm{d}t}\right)^2 [y_{z0}(t)A''(y_{z0},t) + A'(y_{z0},t)] \simeq (y''_{zc})^2\left(\frac{\pi t}{16\sqrt{y_{z0}}} - \frac{\pi t}{8\sqrt{y_{z0}}}\right)(t_c - t)^2 = -\frac{\pi t}{\sqrt{2}}(y''_{zc})^{3/2}(t_c - t), \tag{5.48}$$

$$y_{z0}(t)A'(y_{z0},t)\frac{\mathrm{d}^2 y_{z0}(t)}{\mathrm{d}t^2} \simeq -\frac{\pi t y''_{zc}}{2}\sqrt{y_{z0}} \simeq -\frac{\pi t}{\sqrt{2}}(y''_{zc})^{3/2}(t_c - t).$$

The second derivative $\mathrm{d}^2 y_{z0}(t)/\mathrm{d}t^2$ at $t = t_c$ is denoted by y''_{zc} in the above. The correction ΔC_m also shows the $(t - t_c)$ linear dependence but with positive slope in this case.

$$\frac{1}{N_0 t}\Delta C_m(t) \simeq 3\sqrt{2}\pi(y''_{zc})^{3/2}(t - t_c). \tag{5.49}$$

If we combine (5.49) with (5.33) in the paramagnetic phase, the slope of the T dependence of ΔC_m shows a discontinuous change from positive to negative, resulting in the peak at the critical point. The behavior is observed in numerically calculated results in Fig. 5.2.

As examples of observed temperature dependence of specific heat, the results of the measurements on MnSi by Fawcett et al. [3] and Sc_3In by Ikeda and Gschneidner

[4] are shown in Fig. 5.4. In this figure, values of C/T are plotted against T^2. The dotted (left) and dashed (right) lines plotted by them are regarded as the contribution from lattice vibrations. A clear and definite peak is observed for MnSi with fairly large spontaneous magnetic moment ($t_c \sim 0.13$). Whereas for Sc_3In with tiny spontaneous moment ($t_c \sim 0.01$), the peak is not so clear. The tendency is consistent with the theoretical prediction that the larger the value of t_c, the larger and distinct peak appears as shown in Fig. 5.2 numerically.

5.4 Specific Heat Under the External Magnetic Field

We next show in this section how the temperature dependence of the magnetic entropy and the specific heat is determined in the presence of the external magnetic field. We will particularly deal with the following two subjects.

1. The σ dependence of the entropy and the specific heat under constant temperature.
2. Their temperature dependence under constant static external magnetic field.

As for the first one, we need to confirm that the Maxwell relation is satisfied for the field-induced change of the entropy. Concerning the second one, we need to know how to evaluate the temperature dependence under constant magnetic field in the treatment where σ is regarded as independent variable.

For convenience of our later explanation, note that the σ dependence of $y(\sigma, t)$ and $y_z(\sigma, t)$, and their variations, $\delta y(\sigma, t)$ and $\delta y_z(\sigma, t)$, induced by the external magnetic field are given by

$$\begin{aligned} y(\sigma, t) &= y_0(t) + y_1(t)\sigma^2, \quad y_z(\sigma, t) = y_0(t) + 3y_1(t)\sigma^2, \\ \delta y(\sigma, t) &= y(\sigma, t) - y(0, t) = y_1(t)\sigma^2, \\ \delta y_z(\sigma, t) &= y_z(\sigma, t) - y_z(0, t) = 3y_1(t)\sigma^2, \end{aligned} \tag{5.50}$$

in the paramagnetic phase, and by

$$\begin{aligned} y(\sigma, t) &= y_1(t)[\sigma^2 - \sigma_0^2(t)], \quad y_z(\sigma, t) = 2y_1(t)\sigma_0^2(t) + 3y(\sigma, t), \\ \delta y(\sigma, t) &= y(\sigma, t) - y(\sigma_0, t) = y(\sigma, t), \\ \delta y_z(\sigma, t) &= y_z(\sigma, t) - y_z(\sigma_0, t) = 3y(\sigma, t), \end{aligned} \tag{5.51}$$

in the magnetically ordered phase ($T < T_c$).

5.4.1 *Maxwell Relation*

For the free energy $F(M, T)$ with independent variables M and T, the total differential $\mathrm{d}F$ is written in the form

$$\begin{aligned} \mathrm{d}F(M,T) &= -S_m(M,T)\mathrm{d}T + H(M,T)\mathrm{d}M, \\ -S_m(M,T) = \frac{\partial F(M,T)}{\partial T}, &\quad H(M,T) = \frac{\partial F(M,T)}{\partial M}. \end{aligned} \tag{5.52}$$

The entropy S_m and the magnetic field H are derived by the first derivatives of F with respect to T and M, respectively. Their further derivatives with respect to M and T given by

$$-\frac{\partial S_m}{\partial M} = \frac{\partial^2 F}{\partial M \partial T}, \quad \frac{\partial H}{\partial T} = \frac{\partial^2 F}{\partial T \partial M}, \tag{5.53}$$

agree with each other. It means that the following Maxwell relation is satisfied.

$$\begin{aligned} \frac{\partial S_m}{\partial M} &= -\frac{\partial H}{\partial T} = -M\frac{\partial}{\partial T}\left(\frac{H}{M}\right)\bigg|_M, \\ \frac{1}{N_0}\frac{\partial S_m(\sigma,t)}{\partial \sigma} &= -\frac{2T_A\sigma}{T_0}\frac{\partial y(\sigma,t)}{\partial t}. \end{aligned} \tag{5.54}$$

The second line is the dimensionless form of the first equation in terms of dimensionless parameters, $\sigma = M/2N\mu_\mathrm{B}$, $h = 2\mu_\mathrm{B}H$, $y(\sigma,t) = h/2T_A\sigma$, and $t = T/T_0$. According to (5.50) and (5.51), $\partial y(\sigma,t)/\partial t$ is written in the form

$$\frac{\partial y(\sigma,t)}{\partial t} \simeq \begin{cases} \dfrac{\mathrm{d}y_0(t)}{\mathrm{d}t}, & \text{for } \sigma \simeq 0 \\ -y_1(t)\dfrac{\mathrm{d}\sigma_0^2(t)}{\mathrm{d}t}, & \text{for } \sigma \simeq \sigma_0(t), \end{cases} \tag{5.55}$$

in the paramagnetic (above) and ordered (below) phases. In what follows, we will show the entropy in (5.34) actually satisfies the relation.

In the Paramagnetic Phase With using (5.10), (5.11), and (5.12) for $\Delta y_z(\sigma,t)$, $\lambda(\sigma,t)$, and $\Delta F_1(\sigma,t)$, respectively, the σ dependence of ΔS_m is given by

$$\begin{aligned} T_0\Delta S_m(\sigma,t) &= -N_0T_A\lambda(\sigma,t)\frac{\partial \Delta y_z(\sigma,t)}{\partial t} - \frac{\partial \Delta F_1}{\partial t} \\ &= \frac{3}{5}N_0T_A\frac{\mathrm{d}y_1(t)}{\mathrm{d}t}\sigma^4 + \cdots . \end{aligned} \tag{5.56}$$

This term of higher order correction can be neglected in this case. On the other hand for $S_{m0}(\sigma,t)$, effects of magnetic field on $u(\sigma,t)$ and $u_z(\sigma,t)$ are given by $\delta u(\sigma,t) = x\delta y(\sigma,t)/t$ and $\delta u_z(\sigma,t) = x\delta y_z(\sigma,t)/t$ in terms of variations δy and δy_z. Substituting them into (5.34), the entropy change is therefore represented in the form

$$\begin{aligned}\frac{1}{N_0}\delta S_m(\sigma,t) &= \frac{3}{t}\int_0^1 \mathrm{d}x x^3 u\Phi''(u)[2\delta y(\sigma,t)+\delta y_z(\sigma,t)]\\ &= -3\frac{\partial A(y_0,t)}{\partial t}[2\delta y(\sigma,t)+\delta y_z(\sigma,t)]\\ &= -15 y_1(t)\frac{\partial A(y_0,t)}{\partial t}\sigma^2,\end{aligned}\tag{5.57}$$

by using the relation $2\delta y(\sigma,t)+\delta y_z(\sigma,t) = 5y_1(t)\sigma^2$ in the last line. If we notice the relation (5.32), then (5.57) is finally written as

$$\frac{1}{N_0}\frac{\partial\delta S_m}{\partial\sigma} = -\frac{2T_A\sigma}{T_0}\frac{\mathrm{d}y_0(t)}{\mathrm{d}t}.\tag{5.58}$$

It implies that the Maxwell relation in (5.54) is satisfied for the entropy in the paramagnetic phase.

In the Ordered Phase In this case, the entropy change induced by the applied magnetic field is given by

$$\begin{aligned}\delta S_m(\sigma,t) &= \frac{3N_0}{t}\int_0^1 \mathrm{d}x\, x^3[2u\Phi''(u)\delta y(\sigma,t)+u_z\Phi''(u_z)\delta y_z(\sigma,t)]\\ &\quad + \delta\Delta S_m(\sigma,t),\quad u=\frac{x^3}{t},\quad u_z=\frac{x}{t}(y_{z0}+x^2),\end{aligned}\tag{5.59}$$

where deviations $\delta y(\sigma,t)$ and $\delta y_z(\sigma,t)$ are defined in (5.51). Because $\sigma=\sigma_0$ and $y(\sigma_0,0)=0$ are satisfied in the absence of the field, $\delta y(\sigma,0)=y(\sigma,0)$ is satisfied. If we denote the first term by $\delta S_{m0}(\sigma,t)$, (5.59) is also written in the form

$$\frac{1}{N_0}\delta S_{m0}(\sigma,t) = -3\left[2\frac{\partial A(0,t)}{\partial t}\delta y+\frac{\partial A(y_{z0},t)}{\partial t}\delta y_z\right].\tag{5.60}$$

To evaluate the field effect on $\Delta S_m(\sigma,t)$, let us substitute (5.40) for $\mathrm{d}\lambda(\sigma_0,t)/\mathrm{d}t$ in (5.37). Then the correction is given by

$$\begin{aligned}\frac{1}{N_0}\delta\Delta S_m(\sigma,t) &= 3\left\{\frac{\partial A(y_{z0},t)}{\partial t}+[A'(y_{z0},t)-c]\,\frac{\mathrm{d}y_{z0}}{\mathrm{d}t}\right\}\delta y_z\\ &\quad+\left\{6\frac{\partial A(0,t)}{\partial t}+15cy_1(0)\frac{\mathrm{d}\sigma_0^2(t)}{\mathrm{d}t}\right\}\delta y\\ &\quad-\frac{T_A}{T_0}\frac{\mathrm{d}y_{z0}(t)}{\mathrm{d}t}\delta\lambda(\sigma,t)\\ &= 3\left[\frac{\partial A(y_{z0},t)}{\partial t}\delta y_z+2\frac{\partial A(0,t)}{\partial t}\delta y\right]+\frac{T_A}{T_0}\frac{\mathrm{d}\sigma_0^2(t)}{\mathrm{d}t}\delta y,\end{aligned}\tag{5.61}$$

by using the definition $\Delta y_z\equiv\delta y_z-\delta y$ in (5.37). In the above derivation, we employ the expression (II) for $\mathrm{d}\lambda(\sigma_0,t)/\mathrm{d}t$ in (5.40) in the first line, and (I) in the second line. The following relation for $\delta\lambda(\sigma, t)$ in the third line is also used in the above derivation:

$$\frac{T_A}{T_0}\delta\lambda(\sigma, t) = 2\left\{[A'(y_{z0}, t) - c]\delta y_z - [A'(0, t) - c]\delta y\right\} - \frac{T_A}{3T_0}\delta\sigma^2$$
$$= 3[A'(y_{z0}, t) - c]\delta y_z, \quad (5.62)$$

which is derived from the definition of $\lambda(\sigma, t)$ in (5.9) and the deviation of the condition of TAC, given by

$$2[A'(0, t) - c]\delta y + [A'(y_{z0}, t) - c]\delta y_z + \frac{T_A}{3T_0}\delta\sigma^2 = 0. \quad (5.63)$$

By putting (5.60) and (5.61) into (5.59), the following entropy change is finally obtained:

$$\frac{1}{N_0}\delta S_m(\sigma, t) = \frac{T_A}{T_0}\frac{\mathrm{d}\sigma_0^2(t)}{\mathrm{d}t}\delta y(\sigma, t). \quad (5.64)$$

Partial derivative of the above both sides with respect to σ gives the Maxwell relation:

$$\frac{1}{N_0}\frac{\partial S_m(\sigma, t)}{\partial\sigma} = \frac{2T_A\sigma}{T_0}y_1(t)\frac{\mathrm{d}\sigma_0^2(t)}{\mathrm{d}t}, \quad (5.65)$$

by using $\partial y(\sigma, t)/\partial\sigma = 2y_1(t)\sigma$. As the last term, the right hand side in (5.64) is involved in the entropy correction $\delta\Delta S_m(\sigma, t)$ in (5.61). This clearly means that we need to include this term to satisfy the Maxwell relation in the ordered phase.

5.4.2 Temperature Derivatives in the Static External Magnetic Field

To evaluate the temperature dependence of the specific heat in a constant external magnetic field h, we need temperature derivatives of $y(\sigma, t)$ and $y_z(\sigma, t)$ in this condition. These values are related with derivatives in a constant magnetization σ, as shown below.

To begin with, the derivative of the definition, $y(\sigma, t) = h/2T_A\sigma$, with respect to temperature in a constant σ gives the relation:

$$\left.\frac{\partial y(\sigma, t)}{\partial t}\right|_h = -\frac{h}{2T_A\sigma^2}\left.\frac{\partial\sigma}{\partial t}\right|_h = -\frac{y(\sigma, t)}{\sigma}\left.\frac{\partial\sigma}{\partial t}\right|_h. \quad (5.66)$$

It is also rewritten in the form

$$\left.\frac{\partial y(\sigma, t)}{\partial t}\right|_h = \frac{\partial y(\sigma, t)}{\partial t} + \frac{\partial y(\sigma, t)}{\partial\sigma}\left.\frac{\partial\sigma}{\partial t}\right|_h. \quad (5.67)$$

In the condition of constant h, $\sigma(h,t)$ is regarded as a function of h and t. By equating these relations, (5.66) and (5.67), the following relation between $\partial\sigma/\partial t|_h$ and $\partial y(\sigma,t)/\partial t$ is derived:

$$\left[\frac{y(\sigma,t)}{\sigma}+\frac{\partial y(\sigma,t)}{\partial\sigma}\right]\frac{\partial\sigma}{\partial t}\bigg|_h=\frac{y_z(\sigma,t)}{\sigma}\frac{\partial\sigma}{\partial t}\bigg|_h=-\frac{\partial y(\sigma,t)}{\partial t},$$
$$\therefore\ \frac{\partial\sigma}{\partial t}\bigg|_h=-\frac{\sigma}{y_z(\sigma,t)}\frac{\partial y(\sigma,t)}{\partial t}. \tag{5.68}$$

Then, the temperature derivative of any function $f(\sigma,t)$ in a constant h is generally written as follows:

$$\begin{aligned}\frac{\partial f(\sigma,t)}{\partial t}\bigg|_h&=\frac{\partial f(\sigma,t)}{\partial t}+\frac{\partial f(\sigma,t)}{\partial\sigma}\frac{\partial\sigma}{\partial t}\bigg|_h\\&=\frac{\partial f(\sigma,t)}{\partial t}-\frac{\sigma}{y_z(\sigma,t)}\frac{\partial y(\sigma,t)}{\partial t}\frac{\partial f(\sigma,t)}{\partial\sigma}.\end{aligned} \tag{5.69}$$

Substituting $y(\sigma,t)$ or $y_z(\sigma,t)$ for $f(\sigma,t)$, as special cases we obtain the relations:

$$\begin{aligned}\frac{\partial y(\sigma,t)}{\partial t}\bigg|_h&=\left[1-\frac{\sigma}{y_z(\sigma,t)}\frac{\partial y(\sigma,t)}{\partial\sigma}\right]\frac{\partial y(\sigma,t)}{\partial t}=\frac{y(\sigma,t)}{y_z(\sigma,t)}\frac{\partial y(\sigma,t)}{\partial t},\\\frac{\partial y_z(\sigma,t)}{\partial t}\bigg|_h&=\frac{\partial y_z(\sigma,t)}{\partial t}-\frac{\sigma}{y_z(\sigma,t)}\frac{\partial y(\sigma,t)}{\partial t}\frac{\partial y_z(\sigma,t)}{\partial\sigma}.\end{aligned} \tag{5.70}$$

By using these relations, various temperature derivatives in a constant h can be written in terms of derivatives with respect to σ.

5.4.3 Entropy and Specific Heat in the Paramagnetic Phase

Let us now show the temperature and the external dependence of the entropy and the specific heat.

Effect of Magnetic Field in the Paramagnetic Phase As we have already shown, the entropy change $\delta S_m(\sigma,t)$, induced by the external magnetic field h, is given by (5.57). Actually to evaluate the change in a constant h, we are required to find the value of σ as a function of h.

The magnetic field effect on the specific heat is also given by the temperature derivative of (5.57) under the constant h condition:

$$\begin{aligned}\frac{1}{N_0t}\delta C_m(\sigma,t)&=\frac{1}{N_0}\frac{\partial\delta S_m(\sigma,t)}{\partial t}\\&=-3\frac{\mathrm{d}}{\mathrm{d}t}\left[\frac{\partial A(y_0,t)}{\partial t}\right](2\delta y+\delta y_z)-3\frac{\partial A(y_0,t)}{\partial t}\left[2\frac{\partial\delta y}{\partial t}\bigg|_h+\frac{\partial\delta y_z}{\partial t}\bigg|_h\right]\end{aligned}$$

$$= -3\frac{\mathrm{d}}{\mathrm{d}t}\left[\frac{\partial A(y_0,t)}{\partial t}\right](2\delta y + \delta y_z)$$
$$-3\frac{\partial A(y_0,t)}{\partial t}\left[\left(2\frac{\partial \delta y}{\partial t} + \frac{\partial \delta y_z}{\partial t}\right) - \left(2\frac{\partial \delta y}{\partial \sigma} + \frac{\partial \delta y_z}{\partial \sigma}\right)\frac{\sigma}{y_z}\frac{\partial y}{\partial t}\right], \tag{5.71}$$

by using the relation (5.69) for $f(\sigma, t) = 2\delta y(\sigma, t) + \delta y_z(\sigma, t)$. In what follows, temperature and external field dependence of the entropy and the specific heat are examined in more detail in some particular temperature regions.

Exchange Enhanced Paramagnets at Low Temperatures For paramagnets in the vicinity of the ferromagnetic instability point, the inverse of the magnetic susceptibility (see Sect. 3.3.2) is given by

$$y_0(t) = y_0(0) + \frac{1}{24cy_0(0)}t^2 + \cdots . \tag{5.72}$$

Then, the following result is derived because of the relation between $y_0(t)$ and $\partial A(y_0, t)/\partial t$ in (5.32).

$$y_1(t)\frac{\partial A(y_0,t)}{\partial t} = cy_1(0)\frac{\mathrm{d}y_0(t)}{\mathrm{d}t} \simeq \frac{y_1(0)}{12y_0(0)}t. \tag{5.73}$$

By substituting (5.73) into (5.57), the entropy change is finally given by

$$\frac{1}{N_0}\delta S_m(\sigma,t) = -\frac{5y_1(0)}{4y_0(0)}t\sigma^2 + \cdots . \tag{5.74}$$

In this range of temperature, the entropy $S_m(0, t)$ in the absence of magnetic field shows the same temperature dependence as (5.30) for the specific heat. The sum of these contributions is written as follows:

$$S_m(\sigma,t) = \frac{N_0}{4}t\left[3\log\left(\frac{1}{y_0(0)}\right) - 5\frac{y_1(0)}{y_0(0)}\sigma^2\right] + \cdots . \tag{5.75}$$

It can be also expressed as the T-linear coefficient of the specific heat:

$$\gamma_m(\sigma) = \lim_{t\to 0}\frac{C_m(\sigma,t)}{T} = \frac{1}{T_0}\lim_{t\to 0}\frac{S_m(\sigma,t)}{t} = \frac{3N_0}{4T_0}\left[\log\frac{1}{y_0(0)} - \frac{5y_1(0)}{3y_0(0)}\sigma^2\right], \tag{5.76}$$

or in the form of the relative change of its magnitude.

$$\frac{\Delta C_m(\sigma,0)}{C_m(0,0)} = \frac{C_m(\sigma,0) - C_m(0,0)}{C_m(0,0)} = -\frac{5y_1(0)}{3y_0(0)\log[1/y_0(0)]}\sigma^2$$
$$= -\frac{5}{3}\frac{y_1(0)/y_0(0)}{\log(1/y_0(0))}\left[\frac{h}{T_A y_0(0)}\right]^2 = -\frac{5}{3}\frac{(\chi_0/N_0)^3 F_1}{\log(2T_A\chi_0/N_0)}h^2. \tag{5.77}$$

It is equivalent with the following result by Béal-Monod et al. [5].

$$\frac{\Delta C_m(\sigma,0)}{C_m(0,0)} = -0.1\frac{S}{\log S}\left(\frac{H}{T_{\rm sf}}\right)^2, \quad (S=(1-\alpha)^{-1},\ 1/T_{\rm sf}\propto S\chi^0_{\rm Pauli}),$$

where S and $H/T_{\rm sf}$ correspond to $1/y_0$ and $h/T_A y_0$, respectively, and $\alpha = I\rho$ which appears in the Stoner condition.

In the Region at High Temperatures Except for the region around the critical temperature, the field effect on the inverse of the magnetic susceptibility in (5.71) is well approximated by $\delta y(\sigma,t)+\delta y_z(\sigma,t)\simeq 5y_1(t)\sigma^2$. If we assume that the temperature dependence of the coefficient $y_1(t)$ of the σ^4 term of the free energy is neglected, the following approximation is satisfied.

$$\frac{\mathrm{d}}{\mathrm{d}t}\left[\frac{\partial A(y_0,t)}{\partial t}\right]\simeq \frac{T_A}{15T_0 y_1(t)}\frac{\mathrm{d}^2 y_0(t)}{\mathrm{d}t^2}$$

Because the higher order effect of magnetic field is neglected in this case,

$$\frac{1}{y_z(\sigma,t)}\frac{\partial y(\sigma,t)}{\partial t}\simeq\frac{1}{y_0(t)}\frac{\mathrm{d}y_0(t)}{\mathrm{d}t} \tag{5.78}$$

is justified in the last line. We can therefore obtain the following approximation for (5.71).

$$\begin{aligned}\frac{\delta C_m}{N_0 t} &\simeq -\frac{T_A}{T_0}\frac{\mathrm{d}^2 y_0(t)}{\mathrm{d}t^2}\sigma^2 - \frac{T_A}{5T_0 y_1(t)}\frac{\mathrm{d}y_0(t)}{\mathrm{d}t}\left(5\frac{\mathrm{d}y_1(t)}{\mathrm{d}t}-10\frac{y_1(t)}{y_0(t)}\frac{\mathrm{d}y_0(t)}{\mathrm{d}t}\right)\sigma^2\\ &\simeq -\frac{T_A}{T_0}\sigma^2\left[\frac{\mathrm{d}^2 y_0(t)}{\mathrm{d}t^2}-\frac{2}{y_0(t)}\left(\frac{\mathrm{d}y_0(t)}{\mathrm{d}t}\right)^2\right]=\frac{T_A}{4T_0}\frac{\mathrm{d}^2 y_0^{-1}(t)}{\mathrm{d}t^2}\frac{h^2}{T_A^2},\end{aligned} \tag{5.79}$$

where $\sigma\simeq h/[2T_A y_0(t)]$ is assumed in the last line.

In this region, the field effect gives the positive deviation δC_m proportional to h^2. In the range where the Curie-Weiss law behavior is observed, its coefficient shows the dependence, $t/(t-t_c)^3$. The external field generally suppresses the entropy, and its deviation δS_m is negative. However, its temperature dependence shows the positive slope, giving the positive δC_m.

Around the Critical Temperature In this case, the entropy change $\delta S_m(\sigma,t_c)$ is also evaluated by using the second line of (5.57) with $y_0=0$, i.e.,

$$\frac{1}{N_0}\delta S_m(\sigma,t_c) = -3\left.\frac{\partial A(0,t)}{\partial t}\right|_{t=t_c}[2\delta y(\sigma,t_c)+\delta y_z(\sigma,t_c)]. \tag{5.80}$$

Since $\delta y(\sigma,t_c)=y(\sigma,t_c)$ and $\delta y_z(\sigma,t_c)=y_z(\sigma,t_c)$ are satisfied, substituting the critical isotherm, $\delta y(\sigma,t_c)=y_c\sigma^4$ and $\delta y_z(\sigma,t_c)=5y_c\sigma^4$, gives the following σ

dependence of the entropy:

$$\frac{1}{N_0}\delta S_m(\sigma, t_c) = -21 y_c \frac{\partial A(0,t)}{\partial t}\bigg|_{t=t_c} \sigma^4 = -\frac{28A(0,t_c)}{t_c} y_c \sigma^4, \tag{5.81}$$

by using the relation, $\partial A(0,t)/\partial t = 4A(0,t)/3$, derived from the t dependence, $A(0,t) \propto t^{4/3}$, in (2.86).

The specific heat is evaluated as the critical limit of the expression (5.71) in the paramagnetic phase. We then need to evaluate the σ dependence of derivatives $\partial y(\sigma,t)/\partial t$ and $\partial y_z(\sigma,t)/\partial t$. They are determined by solving the equation:

$$2\frac{\partial A(y,t)}{\partial t} + \frac{\partial A(y_z,t)}{\partial t} + 2[A'(y,t) - c]\frac{\partial y}{\partial t} + [A'(y_z,t) - c]\frac{\partial y_z}{\partial t} = 0, \tag{5.82}$$

which is derived from the temperature derivative of the TAC condition. Because of the predominant $1/\sqrt{y}$ dependence of $A'(y,t)$, it can be approximated by

$$-\frac{\pi t_c}{4\sqrt{y}}\frac{\partial y}{\partial t} - \frac{\pi t_c}{8\sqrt{y_z}}\frac{\partial y_z}{\partial t} + \frac{4}{t_c}A(0,t_c) \simeq 0, \tag{5.83}$$

where the $\sqrt{y}$ and $\sqrt{y_z}$-linear dependence resulting from the first two terms in (5.83) are discarded in the limit, $y \to 0$ and $y_z \to 0$. From the σ^4-linear behavior of $\delta y(\sigma,t)$ and $\delta y_z(\sigma,t)$, the following results are obtained:

$$\frac{\partial \delta y(\sigma,t)}{\partial t} \propto \sigma^2, \quad \frac{\partial \delta y_z(\sigma,t)}{\partial t} = \frac{\partial \delta y(\sigma,t)}{\partial t} + \sigma\frac{\partial \delta y(\sigma,t)}{\partial \sigma} \simeq 3\frac{\partial \delta y(\sigma,t)}{\partial t}. \tag{5.84}$$

The σ^2-linear coefficient determined by (5.83) is given by

$$\frac{\partial \delta y(\sigma,t)}{\partial t} \simeq \frac{32\sqrt{5y_c}}{(2\sqrt{5}+3)\pi t^2}A(0,t)\sigma^2. \tag{5.85}$$

Substituting these results for $\partial\delta y/\partial t$ and $\partial\delta y_z/\partial t$ into (5.71), the effect of the magnetic field on the specific heat is written as follows:

$$\begin{aligned}
\frac{\delta C_m}{N_0 t_c} &= -3\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial A(y_0,t)}{\partial t}\bigg|_{y_0=0}(2y+y_z) + \frac{9}{5}\frac{\partial A(0,t)}{\partial t}\frac{\partial y(\sigma,t)}{\partial t}\bigg|_{t=t_c} \\
&= \frac{384\sqrt{5y_c}}{5(2\sqrt{5}+3)\pi t_c^3}A^2(0,t_c)\sigma^2 + \frac{56}{3t_c^2}A(0,t_c)y_c\sigma^4 + \cdots \\
&= \frac{8A^3(0,t_c)}{t_c^4}\left[\frac{20}{\pi(2+\sqrt{5})}\right]^2\frac{12(5+2\sqrt{5})}{25(2\sqrt{5}+3)}\left(\frac{\sigma}{\sigma_s}\right)^2 + \cdots,
\end{aligned} \tag{5.86}$$

where the coefficient of the first term and the σ derivative of the last term in (5.71) are estimated by

$$
\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial A(y_0,t)}{\partial t}\bigg|_{y_0=0} &= \frac{\partial A'(y_0,t)}{\partial t}\frac{\mathrm{d}y_0(t)}{\mathrm{d}t}\bigg|_{y_0=0} + \frac{\partial^2 A(0,t)}{\partial t^2} \\
&\simeq -\frac{\pi}{8\sqrt{y_0(t)}}\frac{\mathrm{d}y_0(t)}{\mathrm{d}t}\bigg|_{y_0=0} + \frac{4}{9t^2}A(0,t) = -\frac{8}{9t^2}A(0,t) \\
\frac{\sigma}{y_z}\left(2\frac{\partial y}{\partial \sigma} + \frac{\partial y_z}{\partial \sigma}\right) &= \frac{4(2y+y_z)}{y_z} = \frac{28}{5}.
\end{aligned}
$$

5.4.4 External Field Effect in the Ordered Phase

In the ordered phase, since $\delta y(\sigma, t) = y(\sigma, t)$ is satisfied in (5.64), the field effect on the entropy is given by

$$
\frac{1}{N_0}\delta S_m(\sigma,t) = \frac{T_A}{T_0}y(\sigma,t)\frac{\mathrm{d}\sigma_0^2(t)}{\mathrm{d}t} = 15A(0,t_c)\frac{\mathrm{d}U(t)}{\mathrm{d}t}y(\sigma,t), \tag{5.87}
$$

by using the relation (3.12) between the thermal amplitude $A(0, t_c)$ and σ_0^2. The same parameter $U(t) = \sigma_0^2(t)/\sigma_0^2(0)$ defined in (4.21) is also used.

The field-induced change of the specific heat is derived by the derivative of (5.87) with respect to temperature, i.e., as the sum of two contributions:

$$
\begin{aligned}
\frac{1}{t}\delta C_m(\sigma,t) &= \frac{\partial \delta S_m(\sigma,t)}{\partial t}\bigg|_h = \frac{1}{t}[\delta C_{m1}(\sigma,t) + \delta C_{m2}(\sigma,t)] \\
\frac{1}{N_0 t}\delta C_{m1}(\sigma,t) &= 15A(0,t_c)y(\sigma,t)\frac{\mathrm{d}^2U(t)}{\mathrm{d}t^2} \\
\frac{1}{N_0 t}\delta C_{m2}(\sigma,t) &= 15A(0,t_c)\frac{\mathrm{d}U(t)}{\mathrm{d}t}\frac{\partial y(\sigma,t)}{\partial t}\bigg|_h \\
&= 15A(0,t_c)\frac{\mathrm{d}U(t)}{\mathrm{d}t}\frac{y(\sigma,t)}{y_z(\sigma,t)}\frac{\partial y(\sigma,t)}{\partial t},
\end{aligned} \tag{5.88}
$$

where (5.70) is used as the temperature derivative, $\partial y(\sigma,t)/\partial t|_h$, in a constant h for $\delta C_{m2}(\sigma, t)$.

Field Effect on the Specific Heat at Low Temperatures According to (4.2) and (4.26) in Chap. 4, the σ dependence of the inverse of the magnetic susceptibilities and the temperature dependence of $U(t)$ are given by

$$
\begin{aligned}
y(\sigma,t) &= y_1(t)[\sigma^2 - \sigma_0^2(t)] \simeq y_1(0)[\sigma^2 - \sigma_0(0)^2], \\
&= \frac{1}{c}A(0,t_c)\left[\frac{\sigma^2}{\sigma_0(0)^2} - 1\right], \\
y_z(\sigma,t) &= y_{z0}(t) + 3y_1(t)[\sigma^2 - \sigma_0^2(t)],
\end{aligned} \tag{5.89}
$$

$$\simeq 2y_{z0}(0) + \frac{3}{c}A(0, t_c)\left[\frac{\sigma^2}{\sigma_0(0)^2} - 1\right],$$

$$U(t) = 1 - \frac{\alpha_0 t^2}{360A^2(0, t_c)} + \cdots, \quad \alpha_0 = c[(\pi/2)^4 + 5(\pi/2)^2 + 4].$$

Substituting these results for $y(\sigma, t)$ and $U(t)$ into (5.87), the entropy change is written in the form

$$\frac{1}{N_0}\delta S_m(\sigma, t) = -\frac{\alpha_0 t}{12A(0, t_c)}y(\sigma, t) = -\frac{\alpha_0 t}{12c}\left[\frac{\sigma^2}{\sigma_0^2(0)} - 1\right]. \tag{5.90}$$

As for the specific heat, the second contribution δC_{m2} in (5.88) is neglected. The reason is because both $\mathrm{d}U(t)/\mathrm{d}t$ and $\partial y(\sigma, t)/\partial t|_h$ in (5.88) are proportional to t. As a whole, it is proportional to t^2. If we define the T-linear coefficient of the specific heat $\gamma(\sigma) = C_m(\sigma, t)/T$, as with the case of the paramagnetic phase, its change $\delta\gamma_m(\sigma) = \gamma_m(\sigma) - \gamma_m(0)$ is given by

$$\frac{1}{N_0}\delta\gamma_m(\sigma) = -\frac{\alpha_0}{12T_0A(0, t_c)}y(\sigma, t) = -\frac{\alpha_0}{12cT_0}\left[\frac{\sigma^2}{\sigma_0^2(0)} - 1\right], \tag{5.91}$$

by using the relation, $A(0, t_c) = cy_1(0)\sigma_0^2(0)$ in (3.12). In the region of weak magnetic field, the following relation is satisfied between $y(\sigma, t)$ and h.

$$y(\sigma, t) \equiv \frac{h}{2T_A\sigma} \simeq \frac{h}{2T_A\sigma_0(0)}. \tag{5.92}$$

It follows then that $\delta\gamma_m(\sigma)$ is proportional to h, and its coefficient is given by

$$\frac{1}{N_0}\frac{\partial\gamma_m}{\partial h} = \frac{15A(0, t_c)}{T_0}\frac{\mathrm{d}^2U(t)}{\mathrm{d}t^2}\frac{\partial y(\sigma, t)}{\partial h} = -\frac{5\alpha_0}{8T_A^2\sigma_0^3(0)}. \tag{5.93}$$

Around the Critical Temperature According to (4.38) in Chap. 4, the temperature dependence of the reduced spontaneous magnetization squared $U(t)$ is given by

$$\begin{aligned} U(t) &\simeq a_c\left[1 - \left(\frac{t}{t_c}\right)^{4/3}\right], \\ \frac{\mathrm{d}U(t)}{\mathrm{d}t} &\simeq -\frac{4a_c}{3t}\left(\frac{t}{t_c}\right)^{4/3} \to -\frac{4a_c}{3t_c}, \quad (t \to t_c). \end{aligned} \tag{5.94}$$

By putting the above derivative $\mathrm{d}U(t)/\mathrm{d}t$ and $y(\sigma, t_c) = y_c\sigma^4$ into (5.87), the entropy change induced by external magnetic field is given by

$$\frac{1}{N_0}\delta S_m(\sigma, t_c) = 15A(0, t_c)\left(-\frac{4a_c}{3t_c}\right) y_c\sigma^4 = -\frac{20a_c}{t_c} y_c A(0, t_c)\sigma^4. \tag{5.95}$$

From the continuity condition of the entropies, (5.95) and (5.81) in the paramagnetic phase in the limit $t \to t_c$, we have to assume $a_c = 7/5$ in (5.94). It implies $\xi = 1$ for the parameter introduced in (4.14) related to the presence of spin waves in Chap. 4.

In the deviation of the specific heat $\delta C_m(\sigma, t_c)$, the second temperature derivative $\mathrm{d}^2U(t)/\mathrm{d}t^2$ is necessary. We can find its value by expanding $U(t)$ and $V(t)$ in powers of $(t - t_c)$.

$$\begin{aligned} U(t) &= -u_1(t - t_c) - \frac{u_2}{2}(t - t_c)^2 + \cdots, \\ V(t) &= \frac{v_2}{2}(t - t_c)^2 + \frac{v_3}{6}(t - t_c)^3 + \cdots. \end{aligned} \tag{5.96}$$

The above coefficients u_1, u_2, v_2, and so on, are obtained by putting the above expansion into (4.22) and comparing coefficients of terms with the same powers of $(t - t_c)$. For instant, the first coefficient u_1 is given by $4a_c/3t_c$. Then from (5.88) with these parameters, $\delta C_m(h, t_c)$ is evaluated as follows:

$$\frac{\delta C_m(h, t)}{N_0 t} = -15A(0, t_c)\left[u_2 y(\sigma, t) + u_1 \left.\frac{\partial y(\sigma, t)}{\partial t}\right|_h\right]. \tag{5.97}$$

As with the case in the paramagnetic phase, both $y(\sigma, t)$ and $\partial y(\sigma, t)/\partial t$ at $t = t_c$ are positive, and proportional to σ^4 and σ^2, respectively. The above $\delta C_m(h, t)$ thus becomes negative.

We show in Fig. 5.5, numerically calculated temperature dependence of the entropy change $\delta S_m(\sigma, t)$ induced by external magnetic field. The field-induced change of the specific heat is always negative below t_c, for the slope of the entropy is negative as shown in Fig. 5.5. Whereas in the paramagnetic phase, it is positive. Therefore, $\delta C_m(h, t)$ shows the discontinuous change at the critical point $t = t_c$.

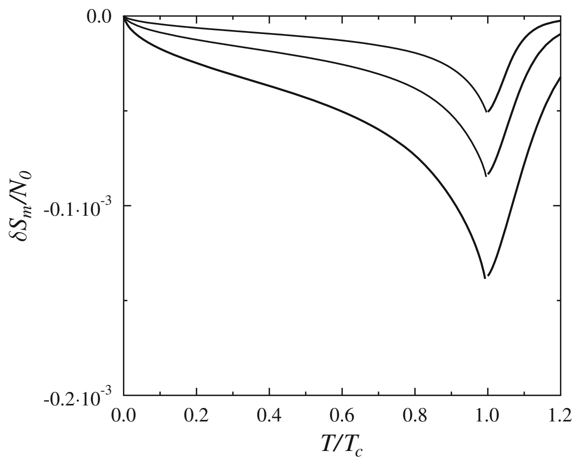

Fig. 5.5 Numerical estimated entropy change for $t_c = 0.1$ under the presence of magnetic field, $h = 0.05$, 0.1, and 0.2 ($\times 10^{-5}$) from the top

5.4.5 Numerical Estimate

To evaluate the entropy and the specific heat at any temperature and in the presence of the external magnetic field of any magnitude h, it is necessary to estimate the values of σ and those of $y(\sigma, t)$ and $y_z(\sigma, t)$ numerically, as well as their temperature derivatives. In the following, we will briefly show how to estimate these values.

Magnetization σ as Independent Variable In this method, we need to evaluate temperature derivatives of various variables as functions of σ. They are evaluated according to the explanation in Sect. 5.4.2. To estimate the value $\partial y(\sigma, t)/\partial t|_h$, for instance, first obtain the value of $\partial y(\sigma, t)/\partial t$, and then by (5.70). The derivative $\partial y(\sigma, t)/\partial t$ is estimated by solving the following simultaneous differential equation for $y(\sigma, t)$ and $\partial y(\sigma, t)/\partial t$ as functions of σ:

$$2A(y, t) + A(y_z, t) - c(2y + y_z) + 5cy_1(0)\sigma^2 = 3A(0, t_c) \tag{5.98}$$

$$2[A'(y, t) - c_z]\frac{\partial y}{\partial t} + [A'(y_z, t) - c_z]\frac{\partial y_z}{\partial t} + 2\frac{\partial A(y, t)}{\partial t} + \frac{\partial A(y_z, t)}{\partial t} = 0. \tag{5.99}$$

The first and the second lines correspond to the TAC condition and its temperature derivative. The functions $y_z(\sigma, t)$ and $\partial y_z(\sigma, t)/\partial t$ are related to $y(\sigma, t)$ and $\partial y(\sigma, t)/\partial t$ by

$$\begin{aligned} y_z(\sigma, t) &= y(\sigma, t) + \sigma\frac{\partial y(\sigma, t)}{\partial \sigma}, \\ \frac{\partial y_z(\sigma, t)}{\partial t} &= \frac{\partial y(\sigma, t)}{\partial t} + \sigma\frac{\partial}{\partial \sigma}\left(\frac{\partial y(\sigma, t)}{\partial t}\right). \end{aligned} \tag{5.100}$$

First σ derivatives of $y(\sigma, t)$ and $\partial y(\sigma, t)/\partial t$ in (5.98) and (5.99) are, therefore, determined by values of σ, $y(\sigma, t)$, and $\partial y(\sigma, t)/\partial t$. The magnetic field h corresponding to σ is determined by $h = 2T_A\sigma y(\sigma, t)$.

Magnetic Field h as Independent Variable On the other hand, it is possible to treat the problem by regarding h as independent variable. In this case, the magnetization $\sigma(h, t)$ is evaluated as a function of h, in place of finding $y(\sigma, t)$ as a function of σ. We then need to evaluate the derivative, $\partial\sigma/\partial t$. They are also evaluated as functions of h by using the same simultaneous equation (5.98) and (5.99).

Note that from the definition of $y(\sigma, t)$ and $y_z(\sigma, t)$, following relations are satisfied among σ, h, and these functions:

$$y(\sigma, t) = \frac{h}{2T_A\sigma}, \quad y_z(\sigma, t) = \frac{1}{2T_A\partial\sigma/\partial h}. \tag{5.101}$$

We can eliminate $y(\sigma, t)$ and $y_z(\sigma, t)$ by substituting (5.101) in (5.98). It is then regarded as the differential equation of σ as the function of h.

For the derivative $\partial\sigma/\partial t$, the t derivative of $y_z(\sigma, t)$ in the above definition (5.101) in a constant h can be written in the form

$$\left.\frac{\partial y_z(\sigma,t)}{\partial t}\right|_h = \frac{1}{2T_A}\frac{\partial}{\partial t}\left(\frac{\partial\sigma}{\partial h}\right)^{-1} = -\frac{1}{2T_A}\left(\frac{\partial\sigma}{\partial h}\right)^{-2}\frac{\partial}{\partial t}\left(\frac{\partial\sigma}{\partial h}\right)$$
$$= -2T_A y_z^2\frac{\partial}{\partial h}\left(\frac{\partial\sigma}{\partial t}\right). \tag{5.102}$$

It is also written by

$$\left.\frac{\partial y_z(\sigma,t)}{\partial t}\right|_h = \frac{\partial y_z(\sigma,t)}{\partial t} + \frac{\partial y_z(\sigma,t)}{\partial\sigma}\left.\frac{\partial\sigma}{\partial t}\right|_h, \quad \left.\frac{\partial\sigma}{\partial t}\right|_h \equiv \frac{\partial\sigma(h,t)}{\partial t} \tag{5.103}$$

by regarding $y_z(\sigma,t)$ as a function of σ and t. By equating the right-hand sides of (5.102) and (5.103), $\partial y_z(\sigma,t)/\partial t$ is given by

$$\frac{\partial y_z(\sigma,t)}{\partial t} = -2T_A y_z^2\frac{\partial}{\partial h}\left[\frac{\partial\sigma(h,t)}{\partial t}\right] - \frac{\partial y_z}{\partial\sigma}\frac{\partial\sigma(h,t)}{\partial t}. \tag{5.104}$$

By substituting (5.68) for $\partial y(\sigma,t)/\partial t$ and (5.104) for $\partial y_z(\sigma,t)/\partial t$, the first and second terms of (5.99) are written in the form,

$$2[A'(y,t)-c]\frac{\partial y(\sigma,t)}{\partial t} = -2[A'(y,t)-c]\frac{y_z}{\sigma}\frac{\partial\sigma}{\partial t}, \tag{5.105}$$

$$[A'(y_z,t)-c_z]\frac{\partial y_z(\sigma,t)}{\partial t} = [A'(y_z,t)-c_z]\left[-2T_A y_z^2\frac{\partial}{\partial h}\left(\frac{\partial\sigma}{\partial t}\right) - \frac{\partial y_z}{\partial\sigma}\frac{\partial\sigma}{\partial t}\right]$$
$$= -2T_A y_z^2[A'(y_z,t)-c_z]\frac{\partial}{\partial h}\left(\frac{\partial\sigma}{\partial t}\right)$$
$$+\left\{2[A'(y,t)-c]\frac{\partial y}{\partial\sigma} + 10cy_{10}\sigma\right\}\frac{\partial\sigma}{\partial t}, \tag{5.106}$$

with using the relation,

$$2[A'(y,t)-c_z]\frac{\partial y}{\partial\sigma} + [A'(y_z,t)-c_z]\frac{\partial y_z}{\partial\sigma} + 10c_z y_{10}\sigma = 0, \tag{5.107}$$

for $\partial y_z/\partial\sigma$, derived from the σ derivative of the TAC condition (5.98). Equation (5.106) is therefore finally written in the form

$$2T_A y_z^2[A'(y_z,t)-c_z]\frac{\partial}{\partial h}\left(\frac{\partial\sigma}{\partial t}\right) = \left\{-2[A'(y,t)-c_z]\frac{y_z-y}{\sigma} + 10c_z y_{10}\sigma\right\}\frac{\partial\sigma}{\partial t}$$
$$+2\frac{\partial A(y,t)}{\partial t} + \frac{\partial A(y_z,t)}{\partial t}. \tag{5.108}$$

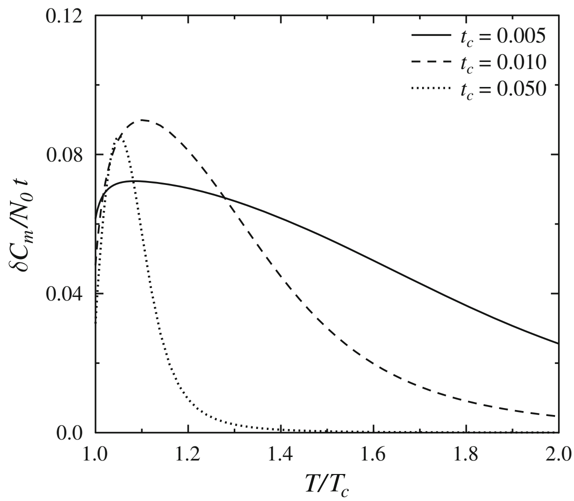

Fig. 5.6 Numerical examples of the temperature dependence of the specific heat change for $t_c = T_c/T_0 = 0.0005$ (*solid*), 0.01 (*dashed*), 0.05 (*dotted*) in the presence of magnetic field

We can now regard (5.98) with (5.101) and (5.108) as the simultaneous differential equation for σ and $\partial\sigma/\partial t$ as functions of h. The initial condition at $\sigma = 0$ in the paramagnetic phase, for instance, is given by

$$2T_A y_0(t)^2 \frac{\partial}{\partial h}\left(\frac{\partial \sigma}{\partial t}\right) = -\frac{\mathrm{d}y_0(t)}{\mathrm{d}t}. \tag{5.109}$$

In this way, we can evaluate $y(\sigma, t)$ and its temperature derivative in (5.88) in a constant h as the functions of h.

Results of Numerical Calculations We have already shown in Fig. 5.5, the temperature dependence of the entropy, i.e., (5.57) and (5.87), in the presence of static external magnetic field. The entropy is always suppressed at any temperature by externally applied magnetic field. It results from the development of the magnetic ordering as the result of the field suppressed fluctuation amplitudes. The temperature dependence of the specific heat is evaluated as the derivative of the entropy with respect to temperature. Characteristic behaviors of Fig. 5.5 are therefore reflected in the temperature dependence of the specific heat. We expect from the steep decreases at low temperatures and around the critical point with increasing temperature in this figure, that the specific heats will show sizable increases of their magnitudes in these regions.

In Fig. 5.6, numerical results of the temperature dependence of the specific heat change in the paramagnetic phase in the constant magnetic field $h = 1.0 \times 10^{-4}$. The values of $\delta C_m/N_0$ are plotted against T/T_c for $t_c = 0.005$, 0.01, and 0.05 by solid, dashed, and dotted lines, respectively. There appear peaks above the critical temperature. Be aware that they are not plotted against T but the reduced temperature T/T_c. Such a peak is actually observed in Sc_3In by Takeuchi and Masuda [2] as shown

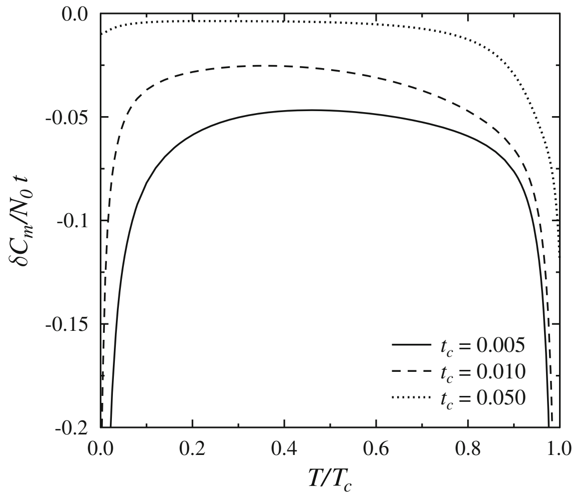

Fig. 5.7 Numerically estimated examples of the temperature dependence of the specific heat change in the ordered phase for $t_c = 0.005$ (*solid*), 0.01 (*dashed*), and 0.05 (*dotted*)

in Fig. 5.1 (right). The peak value is about 2 mJ/K^2 g-atom for $H = 2\,\mathrm{T}$, estimated by assuming that all atoms are magnetic. If we assume only Sc is magnetic and $T_0 = 500\,\mathrm{K}$, the value $T_0(\delta C_m/N_0 T)_{\max} \simeq 0.16$ is obtained. Numerical result by Takahashi and Nakano [6] gives a peak value of 0.1 by using the same values of T_0 and T_A.

Numerically estimated examples in the ordered phase are also shown in Fig. 5.7. They show steep decreases at low temperatures and near the critical temperature reflecting to the corresponding changes of entropies. Widths of them tend to become narrower for smaller t_c. These behaviors result from the second derivative $\mathrm{d}^2U(t)/\mathrm{d}t^2$ in δC_{m1}.

5.4.6 External Field Effect on Paramagnets Near the QCP

According to (5.34), the magnetic entropy of exchange-enhanced paramagnets in the presence of external magnetic field is given by

$$\frac{1}{N_0}S_m(\sigma,t) = -3\int_0^1 \mathrm{d}x x^2\{2[\Phi(u) - u\Phi'(u)] + [\Phi(u_z) - u_z\Phi'(u_z)]\}\{\cdots\} + \frac{1}{N_0}\Delta S_m(\sigma,t), \quad u = x(y+x^2)/t, \quad u_z = x(y_z+x^2)/t. \tag{5.110}$$

Since the correction $\Delta S_m(\sigma,t) \propto \sigma^4$ for paramagnets is neglected in the weak-field region, the specific heat in the presence of external field h is given by

$$\frac{1}{N_0 t} C_m(\sigma, t) = \frac{1}{N_0} \frac{\partial S_m}{\partial t} = -\frac{3}{t} \int_0^1 dx x^2 [2u^2 \Phi''(u) + u_z^2 \Phi''(u_z)] \\ - 6 \frac{\partial A(y, t)}{\partial t} \frac{\partial y}{\partial t}\bigg|_h - 3 \frac{\partial A(y_z, t)}{\partial t} \frac{\partial y_z}{\partial t}\bigg|_h, \quad (5.111)$$

where t derivatives of $y(\sigma, t)$ and $y_z(\sigma, t)$ in a constant magnetic field are evaluated by (5.70). The induced magnetization σ involved in $y(\sigma, t)$ and $y_z(\sigma, t)$ in the right-hand side of (5.111) is determined by solving the magnetic isotherm,

$$y(\sigma, t) = \frac{h}{2T_A \sigma} \simeq y_0(t) + y_1(t)\sigma^2 + \cdots . \quad (5.112)$$

Around the quantum critical point (QCP), the effect of external magnetic field on the specific heat is understood associated with the cross-over between the critical and the low-temperature regions defined in Sect. 3.5.1. Just at the QCP, $t_p = 0$, the T-linear coefficient of the specific heat exhibits the $\log(1/t)$ increase with decreasing temperature toward $t = 0$, as shown in (5.30). It is the characteristic behavior for the critical region, $y/t^{2/3} \ll 1$, because the temperature evolution of $y(0, t) \propto t^{4/3}$ remains unchanged within this region at low temperatures. By applying the external magnetic field, the system will make the transition from the critical to the low-temperature region for $y/t^{2/3} \gg 1$, since the values of $y(\sigma, t)$ and $y_z(\sigma, t)$ become finite, according to (5.112). We will then expect that the critical $\log(1/t)$ behavior of $C_m/N_0 t$ will change into the $\log(1/y)$ behavior at low temperatures. However, with increasing temperature, the system makes the transition into the critical region again, because of the temperature evolution of $y(\sigma, t)$. Therefore, the $\log(1/t)$ behavior will also be recovered.

The above cross-over behavior of the specific heat can be confirmed by numerical studies. In the limit of low temperature, the effect of external field on the last two terms in (5.111) is negligible, since they are higher order corrections with respect to temperature. From the same reason, the magnetic isotherm is approximated by that in the ground state. Numerically estimated temperature dependence of the t-linear coefficient of the specific heats for various external magnetic fields are shown in Fig. 5.8.

5.5 Summary

In this chapter, we have proposed the free energy of the spin fluctuation degrees of freedom, that is consistent with the TAC condition. Based on the free energy, we have shown that the temperature and the external field dependence of the entropy and the specific heat are derived from the unified point of view as summarized below.

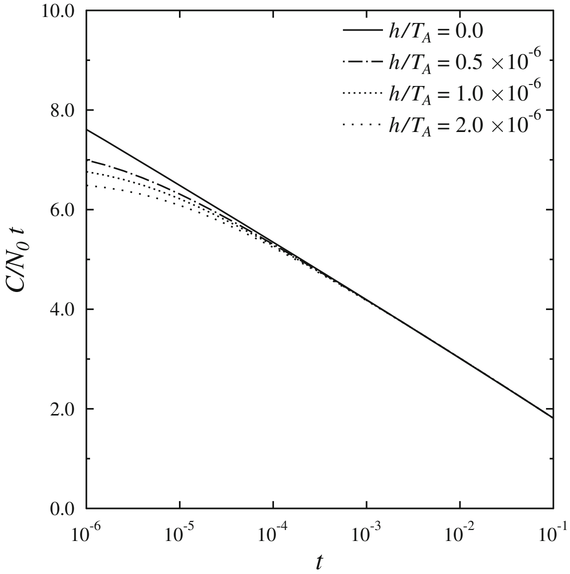

Fig. 5.8 Temperature dependence of the specific heat of a paramagnet at $t_p = 1.0 \times 10^{-4}$ near the QCP in the presence of the external magnetic field

1. Systematic treatment of the entropy and the specific heat becomes possible in predicting various properties even quantitatively through the wide temperature range that can be compared with experiments.
2. Field dependence of our entropy is consistent with the Maxwell relation of the thermodynamics in both the paramagnetic and the ordered phases. As a consequence, the term proportional to $\mathrm{d}^2\sigma_0^2(t)/\mathrm{d}t^2$ is involved in the change of the specific heat in the ordered phase as the effect of externally applied magnetic field.

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