THE SPECIFIC HEAT OF SMALL PARTICLES

WITH A SIZE DISTRIBUTION

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1. INTRODUCTION

In this talk, I should like to discuss an interesting behavior of the specific heat at low temperatures in assemblies of noninteracting small particles. The results are probably quite general but we shall illustrate them with reference to the specific heat of dilute 1D magnets where both the nature of the excitations and the particle size distribution are simple and known.

The arguments run somewhat parallel to Mott's derivation of the $T^2$ law for variable range hopping which it seems appropriate to review briefly in the context of this meeting. In section 3, we give a general derivation for the low temperature specific heat in a d-dimensional system where the elementary excitations behave as $\omega \propto k^p$ with $p = 1$ or 2. In section 4, we apply this to the dilute XY linear chain and to the dilute Heisenberg ferromagnetic and antiferromagnetic linear chain.

2. VARIABLE RANGE HOPPING

In Fig. 1 we show a sketch of an electron moving in a random potential. The density of states in the vicinity of the Fermi level per unit volume is $n_F$ which we assume to be constant over some range of energies. The Fermi energy $E_F$ is assumed to lie in the localized states, below the mobility edge at $E_C$. The conductivity takes place by an electron hopping a distance $R$. There is a factor $\exp(-\alpha R)$ from the overlap of the wavefunctions and the probability of hopping to a level higher in energy by $\Delta$ is $\exp(-\Delta/k_B T)$. In d-dimensions, ignoring factors of $4\pi$ etc., the
average spacing between adjacent energy levels in a sphere of radius $R$ is

$$\Delta = \frac{1}{n_F R^d} \quad (1)$$

so that the conductivity contains a factor

$$\exp[-\alpha R - \Delta/(k_B T)] = e^{f(R)} \quad (2)$$

and

$$f(R) = -\alpha R - \frac{1}{(n_F k_B T R^d)} \quad (3)$$

The prefactor in front of the exponential varies more slowly with distance and is ignored in what follows [In fact it is replaced by its most probable value as determined below]. This greatest contribution from (2) comes when $f(R)$ is a maximum. This occurs when

$$\frac{df}{dR} = 0$$

i.e. $-\alpha + d/(n_F k_B T R_0^{d+1}) = 0$

so that

$$R_0 = \frac{1}{d/(\alpha n_F k_B T)}^{d+1} \quad (4)$$

and

$$f(R_0) = -(T_0/T)^{d+1} \quad (5)$$
with
\[ T_0 = d(2\alpha)^{d+1}/(\alpha n_p) \] (6)

This leads to a conductivity \( \sigma \)
\[ \sigma = \sigma_0 \exp[-(T_0/T)^{d+1}] \] (7)

where \( \sigma_0 \) is only weakly dependent on temperature compared to the exponential. This leads to the famous Mott \( T^k \) variable range hopping law in 3d, which has been observed in a number of systems\(^1\) although it is often difficult to say if the power is precisely 0.25 with data over a limited range of temperatures.

The important aspect of the argument is that the \( \exp(-dR) \) term is large for small \( R \) whereas the \( \exp[-1/(n_p k_B T R^d)] \) term is large for large \( R \). The maximum contribution comes at \( R = R_0 \) which represents a compromise. In 2D, this leads to a \( T^{1/3} \) law and in 1D to a \( T^{1/2} \) law (from equation 7). The above arguments are not rigorous but are believed to lead to the correct answer.\(^1,2\)

3. GENERAL DERIVATION

Consider a finite system where the excitations that control the low temperature specific heat behave as \( \omega \sim k^p \) where \( p = 1 \) for phonons and spin waves in antiferromagnets and \( p = 2 \) for spin waves in ferromagnets. At low enough temperatures, the specific heat is dominated by transitions from the ground state to the first excited state where
\[ \Delta E = a/R^p \] (8)

and \( a \) is some constant. Thus the specific heat will contain a factor
\[ \exp[-a/(k_B T R^p)] \] (9)

At low enough temperatures we will get the Boltzmann factor (9) even if the excitations obey Bose or Fermi statistics. Suppose the probability of obtaining a particle with radius \( R \) is proportional to
\[ \exp[-b R^d] \] (10)

then the specific heat will contain a factor
\[ e^{f(R)} \] (11)

where
\[ f(R) = -b R^d - a/(k_B T R^p) \] (12)
As in the Mott argument there is a trade-off between the higher probability of smaller particles existing but the larger particles having smaller energy gaps. Proceeding as before

\[ \frac{df}{dR} = 0 \]

leads to

\[ R_0 = \left[ \frac{(pa)/(b_dk_BT)}{d+p} \right]^{d+p} \]  \hspace{1cm} (13)

and

\[ f(R_0) = -(T_0/T)^{d+p} \]  \hspace{1cm} (14)

where

\[ T_0 = a b^p/d [p/d(1+d/p)^{1+p/d}] \]  \hspace{1cm} (15)

and so may be rewritten as

\[ R_0 = (T_0/T)^{d+p} [b(1+d/p)]^{-1/d} \]  \hspace{1cm} (16)

Thus the specific heat at low temperatures should behave as

\[ C = C_0 \exp[-(T_0/T)^{d+p}] \]  \hspace{1cm} (17)

where \( C_0 \) is a slowly varying function of temperature. In section 4 we will make these arguments more rigorous and also determine \( C_0 \) for dilute 1D magnetic systems.

For any system with an energy gap \( \Delta E \) between the ground state and first excited states, the specific heat is given by

\[ \frac{C}{k_B} = \frac{g_1}{g_0} (8\Delta E)^2 \exp(-\beta\Delta E) \]  \hspace{1cm} (18)

at sufficiently low temperatures where \( g_0 \) and \( g_1 \) are the degeneracies of the ground state and first excited state. We emphasize that the result (18) is true for Fermions, Bosons or classical particles.

4. ONE-DIMENSIONAL DILUTE MAGNETS

We consider the application of the previous rather general result (17) to 1D magnets. These are simple because the nature of the excitations is known in many cases and the probability distribution of finding a segment of 1 spins (see Fig. 2) is given by
Fig. 2. Showing segments with $r = 2, 3, 4$ in a 1D dilute magnetic system.

$$P_r = N(1-c)^2 c^r$$  \hspace{1cm} (19)$$

where $c$ is the probability of a site being occupied by a spin and $N$ is the total number of available sites in the chain. At sufficiently low temperatures the specific heat is given by

$$C = N(1-c)^2 \sum_{r=1}^{\infty} c^r \left( \frac{\delta A}{r^P} \right)^2 \exp \left( - \frac{\delta A}{r^P} \right)$$  \hspace{1cm} (20)$$

where we have used (18) with $g_0 = g_1 = 1$ and the excitation spectrum (which can obey classical, Fermi or Bose statistics) has the dispersion relation $\omega \sim k^P$ and $A$ is a constant with the dimensions of energy. Identifying the exponential part of (20) as $\exp(f(r))$ we have $f(r)$ given by

$$f(r) = -\alpha r - a/(k_B T r^P)$$  \hspace{1cm} (21)$$

and $\alpha = \ln(1/c)$. Following the steepest descent argument of the previous section leads to

$$r_0 = \left( \frac{pA/\alpha k_B T}{1+P} \right)^{1+P}$$  \hspace{1cm} (22)$$

$$r_0 = \left( \frac{T_0}{T} \right)^{1+P} \left[ \alpha(1 + 1/P) \right]^{-1}$$  \hspace{1cm} (23)$$

where

$$T_0 = pA \alpha^P (1 + 1/P)^{1+P}$$  \hspace{1cm} (24)$$

Replacing the non-exponential part of (20) that contains $r$ by $r_0$ we find that

$$\frac{C}{Nk_B} = B(T_0/T)^X \exp[-(T_0/T)^Y]$$  \hspace{1cm} (25)$$
where
\[ x = \frac{5y}{2} \]  
(26)

and
\[ y = (1+p)^{-1} \]  
(27)

and
\[ B = \left[ (1-c)^2 \sqrt{2\pi p} \right]/[\alpha(1+p)^3] \]  
(28)

This expression (25) is valid if \( r_0 \gg 1 \) so that the sum may be replaced by an integral. This leads to the condition
\[ \frac{1}{(T/T_0)^{1+p}} \ll \left[ \alpha(1+1/p) \right]^{-1} \]  
(29)

Also the width \( \Delta r \) of the Gaussian in the steepest descent integrand must obey
\[ \Delta r \ll r_0 \]

which leads to the condition
\[ \frac{1}{(T/T_0)^{2(1+p)}} \ll \sqrt{p} \]  
(30)

Both (29) and (30) can be roughly expressed as \( T \ll T_0 \) which is then the region of validity of (25). We will now apply the above formalism to three specific cases

a) The Dilute XV Model

The Hamiltonian is given by
\[ H = J \sum_i \left( S_i^x S_{i+1}^x + S_i^y S_{i+1}^y \right) \]  
(31)

and can be transformed into a non-interacting Fermi Hamiltonian using the Jordan-Wigner transformation.\(^3,4,5\) The Fermi excitations have the dispersion relation
\[ \omega = J \cos k \]  
(32)

with
\[ k = \frac{n\pi}{(r+1)}, \; n = 1, 2 \ldots r. \]  
(33)
for an \( r \) spin segment. The Fermi level is at \( \omega = 0 \) so that

\[
E = \begin{cases} 
\frac{J\pi}{2(r+1)} & \text{for } r \ \text{even} \\
\frac{J\pi}{(r+1)} & \text{for } r \ \text{odd}
\end{cases}
\]

Thus the **even** chains determine the low temperature specific heat which is of the form (25) with

\[
x = \frac{5}{4} \\
y = \frac{1}{2} \\
B = \left[ (1-c)^2 \sqrt{2\pi} / [8 \ln(1/c)] \right] \\
T_0 = 2\pi J \ln(1/c)
\]

There are no additional prefactors as the extra factor 1/2 due to only the even chains contributing is cancelled by a factor 2 because there are both particle and hole excitations. In Fig. 3 we show a plot of this asymptotic form (25) with (35) against the exact answer obtained by summing up the contributions to the specific heat for segments of length \( r \) with 1 \( r \) \( < \) 500. [Note that an extra 4 is included in the definition of \( T_0 \) compared to reference 5.]

These results can be understood in terms of a Fermi hole. The specific heat of this Fermi system may be obtained by integrating over the density of states \( n(E) \) given by

\[
n(E) = N(1-c)^2 \sum_{r=1}^{\infty} \sum_{n=1}^{\infty} \delta(E - \frac{an}{r}) e^{-\alpha r}
\]

\[
= \frac{N(1-c)^2}{a} \left[ \frac{a}{E} \left( e^{\frac{a}{2E}} - e^{-\frac{a}{2E}} \right) \right]^{-2}
\]

where \( \alpha = \ln(1/c) \) and \( a \) is a constant with units of energy. Only the \( n=1 \) excitations contribute to the low temperature specific heat but we keep them all and perform the summations. At large \( E > \alpha a \), we have

\[
n(E) \rightarrow n_0(E) = \frac{N(1-c)^2}{\alpha^2 a}
\]
Fig. 3. Showing a plot of the logarithm of the specific heat versus $y = T_0/(4T)$ for the XY model discussed in section 4 where $T_0$ is defined by equation (35).

so that

$$\frac{n(E)}{n_0(E)} = \left[ \frac{\alpha a}{2E} \left( e^{\frac{2E}{T}} - e^{\frac{a}{2E}} \right) \right]^2$$

(38)

which is plotted in Fig. 4. The specific heat is obtained by multiplying $n(E)$ by the temperature derivative of the Fermi function $f(E)$ and integrating. Because the density of states is zero at the Fermi level, there is no linear term in the specific heat and the main contribution comes from states near but not at the Fermi level. There is a similar density of states for the odd length segments but with a Fermi hole twice as wide. The Fermi hole is really just two Lifshitz tails, one for particles and one for holes.
Fig. 4. Showing the "Fermi Hole" in the dilute XY linear chain where the units of energy are $E/a$ [see equations (36)-(38)] and the density of states $n(E)/n_0(E)$ is from equation (38). The full width in energy $\delta$ of the Fermi hole is $\delta = 2a\ln(1/c)$ which of course tends to zero as $c \to 1$ and is proportional $(1-c)$ for small $(1-c)$.

b) The Heisenberg Antiferromagnet

The Heisenberg spin $S$ antiferromagnet has the Hamiltonian

$$H = J \sum_i \vec{S}_i \cdot \vec{S}_{i+1}$$

(39)

and the excitations are given within spin wave theory by

$$\omega = 2JS \sin k$$

(40)

with $k = \pi n/r$, $n = 0,1,2 \ldots , (r/2 - 1)$. for even chains

$$k = \pi (n+\frac{1}{2})/r$$, $n = 0,1,2 \ldots , (r/2 - 3/2)$. for odd chains

All the modes for even and odd chains are doubly degenerate and there is an additional zero frequency mode for odd chains to give a total of $r$ states in each case. Therefore only odd segments contribute to the low temperature specific heat $\gamma$ given by (25) with

$$x = 5/4$$

$$y = 1/2$$

$$B = [(1-c)^2/2\pi]/[\ln(1/c)]$$

(41)

$$T_0 = 4JS\pi \ln(1/c)$$
This result is very similar to the XY chain. It is not exact for the Heisenberg antiferromagnet although the form is probably correct. For $S = 1/2$, the spin waves have the same form as (40) but with an additional factor $\pi/2$. Note that the result (25) is correct within the spin wave approximation, as only the odd chains contribute giving a factor $1/2$ but the spin waves are doubly degenerate giving a compensating prefactor of $2$.

In Fig. 5, we show the specific heat for various concentrations for the Heisenberg antiferromagnet, using spin wave theory and summing up the contributions for chains of lengths up to 200 spins. The exponential behavior can be seen for $k_B T/2JS < 0.1$. For $c = 1$, the specific heat is linear. At higher temperatures spin wave theory breaks down because of interactions between the magnons.

c) The Heisenberg Ferromagnet

The Hamiltonian is given by (39) with $J \rightarrow -J$ and the exact spin wave dispersion is given by

$$\omega = 2JS(1 - \cos k)$$

with

$$k = \frac{n \pi}{r}, \quad n = 0, 1, 2 \ldots r - 1.$$  

leading to $p = 2$ and a specific heat given by (25) with

$$\begin{align*}
  x &= 5/6 \\
  y &= 1/3 \\
  B &= \left[2(1-c)^2 \sqrt{\pi} \right]/[27\xi(1/c)] \\
  T_0 &= \left(27/4\right) JS\pi^2 [\xi(1/c)]^2
\end{align*}$$

The exponents $x, y$ are different from the two previous cases because of the quadratic dispersion relation (42) at small $k$. We believe the results (25) and (44) are probably exact for the Heisenberg ferromagnet. The spin wave states are exact eigenstates with degeneracy $g_1 = 2rS - 1$ because of the full rotational symmetry of the Heisenberg Hamiltonian. Thus $g_1/g_0 \rightarrow 1$ for large $r$ (see equation 18). While it is known that the multimagnon bound states lie below the spin waves states in energy, nevertheless finite chain calculations for $s = 1/2$ and $r = 8$, show that the lowest excited state always lies on the spin wave branch. This is because the low $k$ states are "pushed out" on the multimagnon branches. However a rigorous proof of this statement is lacking and so we cannot say that (25) is rigorously correct for the Heisenberg Ferromagnet as it is for the XY chain.
Fig. 5. Showing the specific heat of the Heisenberg antiferromagnet for various concentrations obtained by summing up the contributions from chains of length up to 200 spins and using spin wave theory.\(^7\)
5. CONCLUSIONS

We have shown that an unusual low temperature specific heat is predicted for small particles with a size distribution. This should manifest itself in the phonon contribution to the specific heat in powders, the contributions from finite clusters to the specific heat in dilute spin systems etc.

We have shown in detail how this behavior is obtained for the dilute XY chain, and the Heisenberg antiferromagnet and ferromagnet. The form of the result depends on the form of the dispersion relation (i.e. whether it is linear or quadratic) but not on statistics (i.e. whether the quasi-particles are classical, Fermions or Bosons). Although this effect has not yet been seen it should be observable in such systems as Pr(C$_2$H$_5$SO$_4$)$_3$·9H$_2$O with Sm ions substituted for Pr [dilute XY chain] and TMMC doped with Cu [essentially a dilute Heisenberg antiferromagnet]. It will probably be some time before these kinds of effects can be searched for in powders. Even the straightforward exponential behavior expected when all the particles are the same size has not yet been seen experimentally. The magnetic systems look like much more promising candidates.

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REFERENCES

10. J. Bonner, private communication, believes that the first excited state always lies on the spin wave branch and has $\Delta E = JS^2/r^2$ for an $r$ spin segment (open ends) with $S = 1/2$. This is based on the numerical evidence of calculations with finite clusters with $r \leq 11$. We speculate this may be true for all $r$.