Generalized Curie-Weiss law

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It is demonstrated that the susceptibility of the Heisenberg model of magnetism very closely follows a power law in the high-temperature limit as well as in the limit of the Curie temperature. In the high-temperature region the exponent is a function of coordination number and spin value. The discussion is limited to isotropic three-dimensional systems. The analysis should be useful for the extraction of magnetic moments from experimental data.

For most of this century experimentalists have used the Curie-Weiss law to extract magnetic moments from the susceptibility at high temperatures. In the limit of high temperature the Curie-Weiss law would be applicable to a material with an infinite range of interaction. It is not valid even in the limit of high temperature for real materials which have a finite range of interaction, but there is a generalization of the Curie-Weiss law which is valid over a range of temperatures for real materials which are described by the Heisenberg model of ferromagnetism above the Curie temperature T_C.

At high temperatures one expresses the susceptibility of a Heisenberg ferromagnetic system as a series in the inverse temperature. As many as ten terms of this series have been calculated for particular lattices and values of the spin per atom. It is demonstrated here that these series can be generated with very remarkable precision with only two fitting parameters. This should be of interest to fellow experimentalists who desire to extract magnetic moments and information about the exchange interactions from measurements above the Curie temperature T_C.

The high-temperature expansion for the susceptibility of an isotropic system may be expressed as

$$\frac{\chi T}{T_0}=1+\frac{T_p}{T}+\sum_{n=1}^{\infty}(a_n/a_1^n)(T_p/T)^n\,, \tag{1}$$

where $T_0=N_0g^2\mu_B^2S(S+1)/3k$ is Curie's constant. $T_p=a_1J/k$ is the paramagnetic Curie-Weiss temperature, and the constants a_n are known exactly to some order n (see the review of Rushbrooke, Baker, and Wood[1] and the later critical discussion by Camp and Van Dyke[2]. If we take the function

$$\begin{aligned}(1-T^*/T)^{-\gamma^*}&=1+\sum_{n=1}^{\infty}\prod_{j=1}^{n}(T^*/T)\{[\gamma^*+(j-1)]/j\}\\&=1+\gamma^*T^*/T+(1+1/\gamma^*)(\gamma^*T^*/T)^2/2\\&\quad+(1+1/\gamma^*)(1+2/\gamma^*)(\gamma^*T^*/T)^3/6\\&\quad+\cdots\,,\end{aligned} \tag{2}$$

and expand it out to the ninth power of T^*/T, it can be made to agree remarkably well with the nine known terms of Eq. (1) for the fcc lattice with nearest-neighbor interactions for spin $\frac{1}{2}$. The power γ^* is quite close to $\frac{3}{2}$ for this case. The best-fit value is 1.5185. If the fit is made so that the two truncated series expressions agree exactly at $T^*/T=\frac{1}{2}$; then the maximum deviation between Eqs. (1) and (2) between $T^*/T=0$ and the fitted point is 4 parts in 100 000. For $T^*/T>\frac{1}{2}$, the deviation increases to a maximum of 1% at $T^*/T=1$, the apparent Curie temperature.

A simple appeal to universality does not explain this result. This is the application of power laws to the high-temperature limit with different results for each lattice depending upon the effective coordination number. There is a strong connection to methods which use ratios of the successive terms in the high-temperature expansion in order to extract the behavior in the limit of the critical temperature. The fact is that the ratios give evidence of power-law behavior even with the leading terms in the series. The choice of the fcc Heisenberg spin-$\frac{1}{2}$ model to make the point is a bit misleading, for there is something especially well behaved about this series. The power $\frac{3}{2}$ is also what can be extracted from the Padé-approximant analysis to determine the critical-point behavior.[2] Other lattices and other spin values for this and other lattices do not show that special behavior. They all do show power-law behavior at high temperatures as well as at the critical point, but generally the powers are not the same. There is no reason for expecting universality at high temperature and, indeed, it is not observed; but the power law is, and its exponent reflects both the value of the magnetic moment and the number of neighbors coupled to that moment.

In the method of Padé approximants[1] the series given by Eq. (1) are generally written as

$$\begin{aligned}(\chi T/T_0)^{1/\gamma}&=\left[1+\sum_n a_nx^n\right]^{1/\gamma}\\&=\frac{(x-a)(x-b)(x-c)(x-d)(x-e)\cdots}{(x-h)(x-k)(x-l)(x-m)\cdots}\,,\end{aligned} \tag{3}$$

where

$$x = J/kT = T_p/a_1 T \ , \tag{4}$$

J is the exchange constant, and γ is the universal constant for isotropic three-dimensional systems with a finite range of interaction. The last term represents the entire class of Padé approximants. Its numerator has zeros and its denominator has poles in the complex plane which characterize the Padé approximant. The smallest positive real pole is the apparent Curie temperature. It depends, of course, on the choice of γ, but one can vary γ to find the "best" fit. This is never a completely satisfactory procedure.[2] Any of the Padé approximants can be used to give the temperature dependence of the susceptibility over the entire range above the Curie temperature. Unfortunately, they are seldom published and, as far as is known, are not used by experimentalists to analyze their results away from T_C. A best fit is found from the expansion of the Padé approximant to the same order as the expansion of the high-temperature series raised to the power $1/\gamma$. The rest of the terms in the Padé polynomial are evaluated at $x = x_c$, the apparent (inverse) Curie temperature, to give

$$(\chi T/T_0)^{1/\gamma} = x_1/(x_c - x) = (x_1/x_c)/(1 - T_C/T) \tag{5}$$

as the behavior near the critical point. All this is rather amazing as an extrapolation procedure, for the asymptotic form of Eq. (5) only approaches the original series for $T_C/T < \frac{1}{2}$. Nevertheless, the results of such analysis have been used to support the proper preconception of universality in the limit of the critical temperature. It is important to note that the asymptotic power law generally has a value of x_1/x_c which is not equal to 1. This shows that this critical phenomena power law does not hold up to $T_C/T = 0$ where $\chi T/T_0 = 1$. However, there is another power law which fits the high-temperature expansion in the high-temperature limit, not as an extrapolation formula but as an approximation formula. This follows from the similarity of the series expansions of Eqs. (1) and (2). We call this the generalized Curie-Weiss law:

$$\chi T/T_0 = (1 - T^*/T)^{-\gamma^*} \ . \tag{6}$$

For $\gamma^* = 1$, one recovers the Curie-Weiss law with $\gamma^* T^* = T_p$, but γ^* is not unity unless the system has an infinite-range interaction.

There are but two parameters to match series of up to ten terms. This is a (0,1) Padé approximant to Eq. (3) with $x_1 = x_c$. Only the variables γ (now γ^*) and x_c are used for fitting the high-temperature series. This can be done in several ways.

The high-temperature series for the Heisenberg spin-$\frac{1}{2}$ model on the fcc lattice with just nearest-neighbor interactions has the unique property that the x_1/x_c in Eq. (5) is very close to 1, and the same power law holds rather well over the entire region from $T_C/T = 1$ to $T_C/T = 0$. For the bcc Heisenberg spin-$\frac{1}{2}$ model the best-fit high-temperature power is 1.63, while the asymptotic law for the Curie-temperature region appears to extrapolate to 1.38. Note that the disagreement between the apparent extrapolated power laws for fcc and bcc spin-$\frac{1}{2}$ models are a bit outside the limits that one might be willing to set on the basis of the analysis of any individual high-temperature series. Yet the argument for universality of the critical exponents is so compelling this can only be a comment on the difficulty of extrapolation from so far from the Curie temperature. Based on extrapolations from all the various three-dimensional cubic lattices, one could take $\gamma = 1.44 \pm 0.07$ as the universal value for isotropic three-dimensional systems with a finite range of interaction, but it seems a reasonable convention to assume $\gamma = \frac{7}{5}$.

In fitting a power law to a series it is sufficient to have three terms in that series. Whether it then fits over a larger region depends on the nature of the series. As a first approximation, the parameters T^* and γ^* can be taken directly from the first two coefficients, a_1 and a_2. Equation (6) becomes

$$\chi T/T_0 = [1 - (1/\gamma_p)(T_p/T)]^{-\gamma_p} \ , \tag{7}$$

where the Curie-Weiss temperature for nearest-neighbor interactions J_1 is

$$T_p = a_1 J/k = \tfrac{2}{3} q S(S+1) J_1/k \ , \tag{8}$$

where q is the coordination number of the cubic lattice, and

$$\begin{aligned} 1/\gamma_p &= 2a_2/a_1^2 - 1 \\ &= 1 - (2/q)[1 + 3/4S(S+1)] \ . \end{aligned} \tag{9}$$

These equations are readily deduced from the tables in the appendices of Ref. 1. The coordination numbers are sc = 6, bcc = 8, fcc = 12, bcc(1,2) = 14, and fcc(1,2) = 18, where the notation (1,2) means equal first- and second-neighbor interactions. The results for lattices with first- and second-neighbor interactions with arbitrary values are summarized in Ref. 1. One can generalize to obtain an effective q and an effective qJ for longer-range interactions. To obtain the classical limit $S = \infty$, one sets $g^2 \mu_B^2 S(S+1) = m^2$, where m is the moment per atom, and $S(S+1)J = J(\infty)$. The inverse of γ_p goes from $1 - 4/q$ to $1 - 2/q$ as S goes from $\frac{1}{2}$ to ∞. Neither T_0, T_p, nor γ_p are adjustable parameters, except for the fact that they have been fitted using the first three terms of the high-temperature expansion. T_0 is a measure of the magnetic moment. T_p is a measure of the effective exchange interaction qJ, the spin being known from T_0. The paramagnetic power γ_p permits a separation of the coordination number from the exchange parameter. This permits an experimental check on whether or not an interaction is nearest neighbor.

This generalized Curie-Weiss law must hold at sufficiently high temperatures. The values of γ_p are known for many lattices with various ranges of interaction. It takes only the initial terms of the high-temperature series to determine γ_p. The application of experimental data at high temperatures will be treated elsewhere. The argument is not restricted to the Heisenberg model. It can be applied to a general Landau expansion of the free-energy functional with fluctuation contributions to the local

magnetization density. This will be detailed elsewhere.

Table I shows the agreement between the series coefficients as calculated and the values generated using the generalized Curie-Weiss law for each of the coordination numbers. The power series for χ has T_0/T as its leading term. The next term is T_0T_p/T^2. The value of γ_p comes from the third term in the series. In the series for $\chi T/T_0$ expanded in powers of $x=J/kT$, the first term is 1, so it is conventional say that the "first" coefficient is a_1. That is the way the terms are numbered in Table I, although in the form in which I have written Eq. (1) the first two coefficients are both 1.

It is clear from comparing the first column in Table I with the second that the generalized Curie-Weiss law should work quite well at high temperatures. It also suggests that considerable improvement in the fit could be made if T_p and γ_p were to be treated as adjustable parameters to match the series. The results of that analysis, explained below, are also shown in Table I. The parameters g and t are numbers of the order of unity that relate T^* and γ^* to T_p and γ_p; that is,

$$\gamma^*=g\gamma_p, \quad T^*=tT_p/g\gamma_p=tT_p/\gamma^* . \tag{10}$$

Because the improvement in fit is so considerable, it is likely that an experimentalist analyzing data would report

TABLE I. Comparison of terms in series expansion.

Term[a]	Power law γ_p ($g=1, t=1$)	High-temperature expansion	Power law γ^* (best fit)	Parameters g, t
1	1.0	1.0	1.000 447	
2	0.833 333	0.833 333 3	0.829 673	
3	0.648 148	0.638 888 9	0.640 718	fcc($\frac{1}{2}$)
4	0.486 111	0.471 643 5	0.476 522	$\gamma_p=1.5$
5	0.356 481	0.341 821 0	0.346 248	$\gamma^*=1.52$
6	0.257 459	0.245 038 4	0.247 639	$g=1.0134$
7	0.183 899	0.174 063 8	0.175 095	$t=1.0004$
8	0.130 262	0.122 731 8	0.122 732	
9	0.091 666	0.086 021 2	0.086 021	
1	1.0	1.0	1.003 708	
2	0.916 667	0.916 666 7	0.914 821	
3	0.814 815	0.808 333 3	0.801 365	fcc(∞)
4	0.712 963	0.697 106 5	0.688 886	$\gamma_p=1.2$
5	0.617 901	0.592 524 8	0.585 435	$\gamma^*=1.242$
6	0.532 082	0.498 559 7	0.493 692	$g=1.035$
7	0.456 070	0.416 379 0	0.414 019	$t=1.0068$
8	0.389 560	0.345 744 1	0.345 754	
9	0.331 847	0.285 802 1	0.287 803	
10	0.282 070	0.235 369 2	0.238 938	
1	1.0	1.0	0.982 419	
2	0.75	0.75	0.778 631	
3	0.5	0.541 666 7	0.567 840	
4	0.3125	0.374 349 0	0.396 147	bcc($\frac{1}{2}$)
5	0.1875	0.256 543 0	0.268 846	$\gamma_p=2.0$
6	0.109 37	0.172 861 7	0.179 050	$\gamma^*=1.63$
7	0.0625	0.115 557 2	0.117 628	$g=0.815$
8	0.035 156	0.076 489 5	0.076 479	$t=0.9824$
9	0.019 531	0.050 489 5	0.049 321	
10	0.010 742	0.033 128 7	0.031 599	
1	1.0	1.0	0.996 177	
2	0.875	0.875	0.885 054	
3	0.729 169	0.756 264 0	0.754 544	
4	0.592 450	0.630 093 9	0.629 732	bcc(∞)
5	0.473 961	0.521 430 9	0.518 782	$\gamma_p=1.3333$
6	0.375 220	0.424 972 0	0.423 654	$\gamma^*=1.276$
7	0.294 816	0.344 928 5	0.343 796	$g=0.957$
8	0.230 325	0.277 668 3	0.277 668	$t=0.9962$
9	0.179 142	0.222 891 9	0.223 429	
10	0.138 835	0.178 008 7	0.179 250	

[a]It is conventional to label the terms according to the subscript on the a_n's of the high-temperature expansion.

TABLE II. Inverse paramagnetic Curie temperatures.

q	Padé[a] J_1/kT_C	Generalized Curie-Weiss law "Best" fit J_1/kT^*	First three terms $\gamma_p J_1/kT_p$	Curie-Weiss law J_1/kT_p	Powers γ_p	γ^*
			For spin $\frac{1}{2}$			
6	0.595	0.655	1.0	0.3333	3.0	1.89
8	0.396	0.4148	0.5	0.25	2.0	1.63
12	0.249	0.2532	0.25	0.1667	1.5	1.52
14	0.205	0.2058	0.2	0.1428	1.4	1.446
18	0.1475	0.1456	0.1428	0.1111	1.2856	1.315
			For spin infinity			
6	0.346	0.347	0.375	0.25	1.5	1.377
8	0.2435	0.2402	0.25	0.1875	1.3333	1.2766
12	0.1575	0.1542	0.15	0.125	1.2	1.242
14	0.1317	0.1281	0.125	0.107	1.1667	1.2029
18	0.098	0.0955	0.09375	0.0833	1.125	1.15

[a]Reference 11.

the values γ^* and T^* rather than γ_p and T_p/γ_p. It is useful to know the relation between the best-fit values γ^* and T^* and the readily interpretable values γ_p and T_p.

Table II shows the values of J_1/kT_p for each coordination number for the two limits of $S=\frac{1}{2}$ and $S=\infty$. This is compared with $\gamma_p J_1/kT_p$ from the fit to the high-temperature limit, with J_1/kT^* from the best-fit procedure, and, finally, with the estimates of J_1/kT_C from the various studies of the high-temperature series by Padé approximants, Neville tables, etc. That $T^* \approx T_C$ is the result of the analysis. (The figures presented here are those which came out of the analysis before any comparison with T_C.) The very near equality was as much of a surprise as was the degree to which the generalized Curie-Weiss law with free parameters fitted the high-temperature expansion. It turns out that these two things are directly related. The power law that seems to hold in any analysis depends very sensitively on the value chosen for T_C. This is often stated the other way around. In the analysis of the high-temperature series to extract the critical temperature, the result is quite insensitive to the choice of γ. Stated in terms of the generalized Curie-Weiss law with free parameters, it can be said that the apparent paramagnetic Curie temperature T^* is quite close to T_C. It is very much closer than the paramagnetic Curie temperature T_p and somewhat closer than the paramagnetic Curie temperature T_p/γ_p given in Eq. (8).

Because the fitting procedure is so constrained by the

TABLE III. Maximum percent difference of the two truncated series.

q	t	g	Best fit for stated g and t T_C/T ranges 0–0.5	Best fit for stated g and t T_C/T ranges 0–1	Fit for $g=t=1$ T_C/T ranges 0–0.5	Fit for $g=t=1$ T_C/T ranges 0–1
			For spin $\frac{1}{2}$			
6	0.9616	0.63	0.24	−1.7	0.24	3.0
8	0.9824	0.815	0.13	−1.1	0.3	4.5
12	1.0004	1.0133	0.004	−0.1	−0.10	−1.0
14	1.0036	1.0329	−0.023	0.13	−0.14	−1.4
18	1.0033	1.0225	−0.031	0.11	−0.10	−1.1
			For spin infinity			
6	0.9911	0.918	0.05	−0.4	0.36	4.9
8	0.9962	0.957	0.018	−0.045	0.35	4.2
12	1.0067	1.035	−0.09	0.22	−0.16	−2.9
14	1.0051	1.031	−0.055	0.17	−0.18	−2.0
18	1.0049	1.024	−0.07	0.08	−0.14	−1.5

restriction in two parameters, it turns out that γ^* is much more accurately determined for each series than the universal γ is known considering all the series. If Eq. (5) were written as

$$\chi T/T_0=(1-T_C/T)^{-\gamma^*}, \tag{11}$$

where no distinction is made between the real Curie Temperature and the paramagnetic Curie temperature T^*, the discrepancies would begin to be noticeable for $T_C/T>0.6$. For this reason it would be useful to have an expression that fits the critical region as well as the high-temperature region.

The best-fit analysis selects a particular term in the high-temperature series to give the relation

$$t\prod_{m=1}^{S}[1+(m-1)/g\gamma_p]/m=a_S/(a_1)^S \tag{12}$$

between t and g. The value of g is then varied to make the χ's calculated from the two series expansions agree at $T^*/T=\frac{1}{2}$. In this the expansion for the generalized Curie-Weiss law is truncated at the same order to which the high-temperature series is calculated. Generally, S is taken to be an even number, either $n-1$ or $n-2$, depending on whether the series terminates in odd or even n. Table III shows the fractional differences in χ calculated by the two series for the ranges T^*/T from 0 to 0.5 and from 0 to 1. The latter range almost always has its largest error at 1. The best fit is for the fcc ($S=\frac{1}{2}$) case. The poorer, but still very good, fits are for the low coordination numbers with the lowest spin value.

To obtain a formula valid for the entire temperature range (and all spin and coordination numbers) all that is needed is a good "French curve" or a suitable blending function. If one plots the variable Z given by

$$Z=(T_0/\chi T)^{(1/\gamma)} \tag{13}$$

against T_C/T one has a diagonal line running from $Z=1$ for $T_C/T=0$ to $Z=0$ at $T_C/T=1$. It bows slightly to one side or the other of the diagonal, depending on whether γ^* is greater or less than γ. It helps to get a better view of the behavior if one plots $Z/(1-T_C/T)$. This is done in Fig. 1 for the case of bcc spin $\frac{1}{2}$, which lies sufficiently far from the diagonal to show the differences without further expanding the scale. The lines labeled b, c, d, and e are for the high-temperature series truncated at 4, 6, 8, and 10 terms, respectively. The curve labeled f is the generalized Curie-Weiss law with the best-fit values $\gamma^*=1.63$ and $T^*=0.955T_C$. This function, if expanded in the series and truncated at 4, 6, 8, and 10 terms, matches curves b, c, d, and e. Line h is the universal power law, chosen here to be $\gamma=\frac{7}{5}$. Its constant value is the amplitude of the singularity. The behavior away from T_C is such that the amplitude itself increases, starting out with a linear dependence upon $1-T_C/T$, as indicated by the dashed line a. A suitable blend is the function plotted as g. This function has a single parameter which is another version of γ^*. It does not have a variable like T^*. It uses T_C. In a separate publication[3] we set forth this expression, which we believe shows just how the continuous variation from $\gamma_{\text{eff}}=\gamma_p$ to $\gamma_{\text{eff}}=\gamma$ takes place and how it is that the generalized Curie-Weiss law with adjustable parameters works so well.

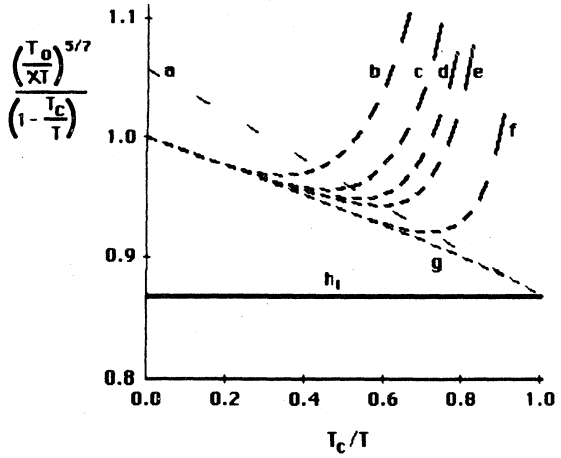

FIG. 1. High-temperature dependence of the susceptibility for the bcc lattice with nearest-neighbor interactions and $s=\frac{1}{2}$. Curves b, c, d, and e use 4, 6, 8, and 10 terms of the high-temperature expansion, respectively. The generalized Curie-Weiss law is curve f. Asymptotic extrapolations of the series, using $\gamma=\frac{7}{5}$, give line h for the leading singularity and line a for two terms of an expansion in $1-T_C/T$ about the critical temperature. Curve g is an extrapolation formula that gives a continuous variation of the effective γ with temperature. Note that a straight line from (0,1) to $(1,h_1)$ comes within 1% of whatever the correct line may be and that $h_1(\gamma_{\text{eff}})$ is known from the lattice type and the spin. Thus $T_0=\chi T[1-(2-h_1)(T_C/T)+(1-h_1)(T_C/T)^2]^{7/5}$ gives a very good value for the moment in analyzing susceptibility data at any temperature above T_C. Even if one did not known h_1, replacing it with 1 would still give a reasonable estimation of the moment.

The temperature dependence of the susceptibility is expressible in terms of T_0, T_p, γ^*, and γ. T_0 and T_p are specified by the model, γ^* is given here in terms of the model parameters $S(S+1)$ and q, and γ is the universal power law which is not precisely known as yet. As mentioned above, experimentalists should find this useful in extracting the magnetic moment, the effective exchange constant, and the coordination number from susceptibility data for any temperature above T_C. If one uses the variables of Fig. 1, the moment is obtained from the high-temperature intercept. If one has an expression for the function g, the effective moment can be obtained for any temperature above T_C.

Note added. Just after this paper was submitted for publication, quite similar observations made by Fähnle and Soultie were published in Ref. 5.

I wish to thank Herbert Capelmann for suggesting that I try to analyze the high-temperature susceptibility results in a manner similar to the approach I used for the temperature dependence of the ferromagnetic region.[4] This work is presented in reverse order, for I started with the plot of Z versus T_C/T. I acknowledge help from Michael Plischke and Bretislav Heinrich, with thanks to both.

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