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Moment Calculations in Lattice Dynamics. I. fcc Lattice with Nearest-Neighbor Interactions

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A new method, using a high-speed computer, is introduced for the evaluation of large numbers of spectral moments for crystals with short-range interactions. As an example, the first 34 even moments are obtained for the fcc lattice with nearest-neighbor central interactions. Accurate algebraic expressions for the thermodynamic properties have been obtained, at all temperatures, by the use of the Padé approximant on the high-temperature moment expansions, together with three terms in the low-temperature expansion. To estimate the order of magnitude of the errors to be expected, the method is applied to a linear chain and the results compared with the exact solution. The fractional error has a maximum of order 2×10^{-4}, and is less than 1×10^{-5} for much of the range. An approximation to the spectrum of the fcc lattice is derived by an orthogonal polynomial expansion.

INTRODUCTION

Much work has been carried out to determine the spectra and thermodynamic properties of crystal models since Born[1] first proposed his theory of lattice vibrations. As the number of models which have been solved exactly[2] is small, most of this work has been concentrated on the approximate methods.

These methods fall into two main groups, the sampling methods and the exact series expansions. The sampling methods enable a histogram approximation of the frequency spectrum to be obtained by evaluating the frequencies at a finite number of points in the Brillouin zone. Blackman[3] first developed this method by using hand calculations. The advent of digital computors, in the 1950's, led many workers[4-6] to carry out extensive sampling calculations. The speed at which these calculations could be performed enabled the accuracy of the spectrum calculation to be increased by an order of magnitude. This provided a simple means of investigating the properties of models, and little attention was given to its possible application to the exact series expansion method.

The sampling methods require the spectrum to be stored, numerically, in the form of a histogram. Therefore, numerical techniques have to be applied to obtain the thermodynamic properties, and the accuracy of the final result is not easy to assess. This makes it difficult to compare related models.

Exact series expansions can be derived at high and low temperatures. At high temperatures, Montroll[7-9] has expanded the thermodynamic properties in terms of the moments of the frequency spectrum. He obtained, by analytical methods, the first seven even moments for a number of ordered cubic models. The moment expansions have none of the disadvantages of the sampling methods and provide the added attraction of an algebraic expansion for both the spectrum and the thermodynamic properties. The main reasons why this method has not been more widely used are (a) the difficulties in obtaining higher moments, and (b) the divergence of the series expansions when $\Theta/T=2\pi$ (where $\Theta=h\nu_{\max}/k$ and T is the temperature), i.e., at low temperatures. The low temperature series expansions are usually restricted to two terms, due to the complexity of the integrals involved.

In this paper a new method is described based on the equivalence, under certain restrictions, of the moments on a finite lattice with those on an infinite lattice. The use of an electronic computer enables the exact value of large numbers of moments to be calculated on the finite lattice, and thence for an infinite lattice. This overcomes difficulty (a).

The divergence of the thermodynamic expansions when $1/T$ becomes large has been overcome by the use of Padé approximants.[10-12] This, together with only one term in the low-frequency expansion, yields an accuracy of over one part in 10^3 at all temperatures. At very low and high temperatures the accuracy is much better. The spectrum can be expanded in an orthogonal set of polynomials whose coefficients are linear combinations of the moments. The optimum convergence of this expansion can be obtained by first obtaining the position and behavior at the critical points in the spectrum,[13,14] and subtracting their contribution from the moments of the spectrum.

At present the fastest computers enable about 100

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[1] M. Born, *Atomtheorie de festen Zustands* (Teubner, Leipzig, 1923).

[2] E. W. Montroll, in *Proceedings of the Third Berkeley Symposium on Mathematical Statistics and Probability* (University of California Press, Berkeley, California, 1956), Vol. 3, p. 209.

[3] M. Blackman, Proc. Roy. Soc. (London) **A148**, 365 and 384 (1934).

[4] E. H. Jacobson, Phys. Rev. **97**, 654 (1955).

[5] C. B. Walker, Phys. Rev. **103**, 547 (1956).

[6] W. C. Overton, National Research Laboratories Report 5252, 1959 (unpublished).

[7] E. W. Montroll, J. Chem. Phys. **10**, 218 (1942).

[8] E. W. Montroll, J. Chem. Phys. **11**, 481 (1943).

[9] E. W. Montroll and D. Peaslee, J. Chem. Phys. **12**, 98 (1944).

[10] G. A. Baker, Jr., Phys. Rev. **124**, 768 (1961).

[11] G. A. Baker, Jr., J. L. Gammel, and J. G. Wills, J. Math. Anal. and Appl. **2**, 21 and 405 (1961).

[12] C. Domb and C. Isenberg, Proc. Phys. Soc. (London) **79**, 3 and 509 (1962).

[13] L. Van Hove, Phys. Rev. **89**, 1189 (1953).

[14] M. Lax and V. L. Lebowitz, Phys. Rev. **96**, 3 (1954).

even moments to be obtained. These calculations require the use of multilength working, on the machine, if all of the information contained in this number of moments is to be extracted. The method is applicable to lattices with complex unit cells and to models with interactions extending to 30 nearest-neighbor atoms. (This limit is set only by the speed of the machine.) Moments could, thus, be derived for all but ionic crystals, where the interactions are long range. The method can also be extended to yield moments on the disordered lattices.

THEORETICAL ANALYSIS

In this section it is shown that under certain conditions the spectral moments on a finite lattice, with cyclic boundary conditions, are equal to those on the infinite lattice.

Consider a lattice made up of $N\times N\times N$ cells each defined by vectors $\mathbf{a}_s$ $(s=1,2,3)$. Then the position of any cell is given by

$$\mathbf{l}=\sum_1^3 l_s\mathbf{a}_s\,,\quad l_s=1,2,\cdots N. \tag{1}$$

Let $\mu_{2n}(N)$ be the $2n$th moment of the spectrum for the finite lattice in which there are interactions between cells for which $l_s\leqslant T$ $(s=1,2,3)$. Then we shall show that,

$$\mu_{2n}(N)=\mu_{2n}(\infty)\quad\text{providing } n<N/T. \tag{2}$$

If $\mathbf{b}_s$ are the vectors of a cell in reciprocal space it is convenient to define

$$\boldsymbol{\tau}=\sum_1^3 h_s\mathbf{b}_s\quad h_s=1,2,\cdots N, \tag{3}$$

where

$$\mathbf{a}_r\cdot\mathbf{b}_s=\delta_{r,s}\,, \tag{4}$$

and

$$\boldsymbol{\theta}=\frac{2\pi}{N}\sum_1^3 h_s\mathbf{b}_s\,, \tag{5}$$

whereupon

$$\boldsymbol{\theta}\cdot\mathbf{l}=\frac{2\pi}{N}\sum_1^3 h_sl_s\,. \tag{6}$$

There are r particles in each cell of which κth and κ'th are typical with masses M_κ and $M_{\kappa'}$, respectively, then the secular equation for the frequencies of the normal modes of this lattice are given by[15]

$$\left|D_{\alpha\alpha'}\begin{pmatrix}\boldsymbol{\theta}\\ \kappa\kappa'\end{pmatrix}-\omega^2\delta_{\alpha\alpha'}\delta_{\kappa\kappa'}\right|=0, \tag{7}$$

where

$$D_{\alpha\alpha'}\begin{pmatrix}\boldsymbol{\theta}\\ \kappa\kappa'\end{pmatrix}=(M_\kappa M_{\kappa'})^{-1/2}\sum_l \Phi_{\alpha\alpha'}\begin{pmatrix}\mathbf{l}\\ \kappa\kappa'\end{pmatrix}\exp(i\mathbf{l}\cdot\boldsymbol{\theta}), \tag{8}$$

in which Φ is the total potential, α and α' are two directions in the crystal, $u_\alpha\begin{pmatrix}\mathbf{l}\\ \kappa\end{pmatrix}$ is the displacement of the κth atom in the $\mathbf{l}$th cell in the α direction, and

$$\Phi_{\alpha\alpha'}\begin{pmatrix}\mathbf{l}\\ \kappa\kappa'\end{pmatrix}=\frac{\partial^2\Phi}{\partial u_\alpha\begin{pmatrix}\mathbf{l}\\ \kappa\end{pmatrix}\partial u_{\alpha'}\begin{pmatrix}\mathbf{0}\\ \kappa'\end{pmatrix}}\,, \tag{9}$$

where this derivative is evaluated at equilibrium. The derivation of equation (7) assumes that the forces are short range, and cyclic boundary conditions are imposed on the lattice. The $2n$th spectral moment of this lattice is defined by

$$\mu_{2n}(N)=\frac{1}{3rN^3}\sum_{\theta,j}\omega_j^{2n}(\boldsymbol{\theta})\,, \tag{10}$$

where ω_j is the jth root of (7). Since the trace of the nth power of a matrix is equal to the sum of the powers of its roots we have

$$\mu_{2n}(N)=\frac{1}{3rN^3}\sum_\theta \operatorname{Tr}\left[D^n\begin{pmatrix}\boldsymbol{\theta}\\ \kappa\kappa'\end{pmatrix}\right]. \tag{11}$$

So that,

$$\mu_{2n}(N)=\frac{1}{3rN^3}\sum_\theta{\sum}' D_{\alpha_i\alpha_j}D_{\alpha_k\alpha_j}\cdots D_{\alpha_m\alpha_i}\,, \tag{12}$$

where the primed sum indicates a sum over all n indices $i, j, k, \cdots m$ of the cyclic product of elements of the D matrix, in which the ith jth elements is $D_{\alpha_i\alpha_j}$. Letting $\prod$ denote the cyclic product of elements $\alpha_i\alpha_j$ this becomes

$$\mu_{2n}(N)=\frac{1}{3rN^3}\sum_\theta{\sum}'\prod D_{\alpha_i\alpha_j}\,. \tag{13}$$

Assuming that interactions occur only between atoms for which

$$l_s\leqslant T\quad s=1,2,3$$

and substituting into (13) for $D_{\alpha_i\alpha_j}$ from (7) we obtain

$$\mu_{2n}(N)=\frac{1}{3rN^3}\sum_\theta{\sum}'\prod\left[(M_\kappa M_{\kappa'})^{-1/2}\times\sum_{l_1,l_2,l_3=-T}^{+T}\Phi\begin{pmatrix}\mathbf{l}\\ \kappa\kappa'\end{pmatrix}\exp(i\mathbf{l}\cdot\boldsymbol{\theta})\right]. \tag{14}$$

We now multiply out the sum over l_1, l_2, l_3, so that each term contains only one exponential term. In order to do this we introduce $\mathbf{l}_{pij}$ where p is the pth term in the expansion of

$$\sum_{-T}^{+T}\Phi_{\alpha_i\alpha_j}\begin{pmatrix}\mathbf{l}\\ \kappa\kappa'\end{pmatrix}\exp(i\mathbf{l}\cdot\boldsymbol{\theta})\,,$$

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[15] A. A. Maradudin, E. W. Montroll, and G. H. Weiss, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Suppl. III.

and the indices i, j refer to this sum. Hence,

$$\mu_{2n}(N)=\frac{1}{3rN^3}\sum_{\theta}\sum{}'\sum{}''\left[\prod(M_\kappa M_{\kappa'})^{-1/2}\right.\\ \left.\times\prod\Phi_{\alpha_i\alpha_j}\begin{pmatrix}\mathbf{l}_{pij}\\ \kappa\kappa'\end{pmatrix}\exp(i\boldsymbol{\theta}\cdot\mathbf{l}_{pij})\right], \quad (15)$$

where $\prod$ is the cyclic product in i and j, and $\sum''$ is the sum over all possible values of p. We can condense the notation by writing

$$\prod\Phi_{\alpha_i\alpha_j}\begin{pmatrix}\mathbf{l}_{pij}\\ \kappa\kappa'\end{pmatrix}=\Lambda\begin{pmatrix}\{\mathbf{l}_{pij}\}\\ \kappa\kappa'\end{pmatrix},$$

and

$$\prod(M_\kappa M_{\kappa'})^{-1/2}=\Gamma(\{\kappa,\kappa'\}).$$

So that,

$$\mu_{2n}(N)=\frac{1}{3rN^3}\sum_{\theta}\sum{}'\sum{}''\Gamma(\{\kappa,\kappa'\})\Lambda\begin{pmatrix}\{\mathbf{l}_{pij}\}\\ \kappa\kappa'\end{pmatrix}\\ \times\exp(i\boldsymbol{\theta}\cdot\textstyle\sum\mathbf{l}_{pij}), \quad (16)$$

where $\sum\mathbf{l}_{pij}$ is the sum over all $\mathbf{l}_{pij}$ occurring in the product $\prod$ in (15). From (6),

$$\mu_{2n}(N)=\frac{1}{3rN^3}\sum_{h_1,h_2,h_3=1}^{N}\sum{}'\sum{}''\Gamma(\{\kappa,\kappa'\})\Lambda\begin{pmatrix}\{\mathbf{l}_{pij}\}\\ \kappa\kappa'\end{pmatrix}\\ \times\prod_{s=1}^{3}\exp\left(2\pi i\frac{h_s}{N}\sum l_{s\,pij}\right) \quad (17)$$

where $\mathbf{l}_{pij}=(l_{1pij},\ l_{2pij},\ l_{3pij})$. Now, providing

$$\sum l_{spij}<N, \quad (18)$$

the sum of the geometric series

$$\sum_{h_s=1}^{N}\exp\left(2\pi i\frac{h_s}{N}\sum l_{spij}\right)=N\delta_{0,\Sigma l_{spij}}. \quad (19)$$

But, we have insured that $l_s\leqslant T$ ($s=1$, 2, 3), i.e.

$$l_{spij}\leqslant T. \quad (20)$$

Hence, as there are only n terms in the sum

$$\sum l_{spij}\leqslant nT.$$

If (19) and (20) are to be satisfied simultaneously, we must have

$$N>nT. \quad (21)$$

Substituting in (17) from (19) finally yields

$$\mu_{2n}(N)=\frac{1}{3rN^3}\sum{}'\sum{}''\Gamma(\{\kappa,\kappa'\})\Lambda\begin{pmatrix}\mathbf{l}_{pij}\\ \kappa\kappa'\end{pmatrix}\\ \times\prod_{s=1}^{3}N\delta_{0,\Sigma l_{spij}}, \quad (22)$$

$$=\frac{1}{3r}\sum{}'\sum{}''\Gamma(\{\kappa,\kappa'\})\Lambda\begin{pmatrix}\mathbf{l}_{pij}\\ \kappa\kappa'\end{pmatrix}\prod_{s=1}^{3}\delta_{0,\Sigma l_{spij}}. \quad (23)$$

This sum is independent of N under condition (21). Thus, the first n even moments on a finite $N\times N\times N$ cell lattice (i.e. excluding $n=0$) are equal to the moments on the infinite lattice, providing

$$n<N/T. \quad (24)$$

The optimum condition occurs when n is equal to the integer which is just below N/T.

This result can be seen more easily by expanding the moments in terms of walks with returns to the origin[15,16] on the lattice. The nth even moments, on the $N\times N\times N$ lattice with cyclic boundary conditions, depends only on the walks which return to the origin in less than $(n+1)$ steps. If the interaction extends between cells, at least one of whose coordinates, (l_1,l_2,l_3) differ by T then the largest step is of size T. The distance covered in any one walk is less than or equal to nT. Now providing, during the course of a walk, we do not completely encircle the lattice i.e., $nT<N$ the result will be the same as on the infinite lattice.

The first n even moments on any infinite lattice can, thus, be calculated, under condition (24) by numerically evaluating the traces of the dynamical matrix, D, for a finite $N\times N\times N$ lattice. This can be accomplished very easily with the use of a digital computer and provides a simple, straightforward, method for obtaining numerous spectral moments.

APPLICATION TO THE fcc NEAREST-NEIGHBOR MODEL

The first seven even moments, on this lattice model, were originally evaluated by Domb and Salter[17] using the results of Montroll[8] on the simple cubic lattice. Montroll expanded the traces of the dynamical matrix algebraically and then summed over all θ values. This method soon becomes cumbersome, and the work involved increases rapidly if further moments are to be obtained. The algebra might be carried out on a computer, but the limitations on the storage space limit the number of moments that may be calculated to about ten.

The secular equation for the fcc lattice has been derived by Leighton[18] and is

$$\begin{vmatrix}2-\cos x(\cos y+\cos z)-\lambda^2 & \sin x\sin y & \sin x\sin z\\ \sin y\sin x & 2-\cos y(\cos x+\cos z)-\lambda^2 & \sin y\sin z\\ \sin z\sin x & \sin z\sin y & 2-\cos z(\cos x+\cos y)-\lambda^2\end{vmatrix}=0, \quad (25)$$

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[16] C. Domb, A. A. Maradudin, E. W. Montroll, and G. H. Weiss, Phys. Rev. **115**, 1, 18, and 24 (1959).

[17] C. Domb and L. Salter, Phil. Mag. **43**, 7 (1952).

[18] R. B. Leighton, Rev. Mod. Phys. **20**, 165 (1948).

where $\lambda^2=2\pi^2m^2/\alpha$, α being the nearest-neighbor force constant, and ν the frequency, and m the mass of an atom.

Also

$$x=\frac{\pi}{N}(-l+m+n)\,,$$

$$y=\frac{\pi}{N}(l-m+n)\,,$$

$$z=\frac{\pi}{N}(l+m-n)\,,$$

where the indices l, m, n, take the values 1, 2, $\cdots N$.

The calculation of the moments requires the evaluation of the sum of the even powers of the roots of this equation for a finite value of N. The number of moments that can be calculated is $(N-1)$ as the interactions are restricted to nearest-neighbor atoms. This calculation can be done most efficiently by storing all the cosines that will be required in the course of the calculation, and then evaluating the first three traces s_1, s_2, s_3 for a point in the Brillouin zone. From these traces all subsequent traces can be calculated by the well-known relationships in the theory of equations[19]:

$$\begin{aligned} s_1+p_1&=0\,,\\ s_2+p_1s_1+2p_2&=0\,,\\ s_3+p_1s_2+p_2s_1+3p_3&=0\,. \end{aligned} \tag{26}$$

For $n>3$

$$s_n+p_1s_{n-1}+p_2s_{n-2}+p_3s_{n-3}=0\,.$$

The three unknown coefficients p_1, p_2, p_3 can be determined from s_1, s_2, s_3 and, thence, one can calculate s_n for $n>3$. Alternatively the roots of the equation can be obtained directly and raised to the appropriate powers.

The calculation can be reduced by a factor of 48 by using the cubic symmetry of the lattice. The secular equation need only be solved in one symmetry element of the Brillouin zone, which is repeated 48 times. The traces of the dynamical matrix, at any point in this element, must be suitably weighted according to its position in the Brillouin zone. For example, points that occur along an edge of the symmetry element will have a different weight from those that are situated in a face. The sum of the weighted traces, at all the points in this element, will give the moments. In practice it is convenient to use the normalized moments u_{2n} defined by

$$u_{2n}=\nu_{\max}{}^{-2n}\int_0^{\nu_{\max}}\nu^{2n}g(x)dx\,, \tag{27}$$

where $x=\nu/\nu_{\max}$ and $g(x)$ is the spectrum or

$$u_{2n}=\int_0^1 x^{2n}g(x)dx\,. \tag{28}$$

The main difficulty encountered in using the moments, for the calculation of the spectrum and other properties, is that the higher moments are heavily weighted with respect to one end of the spectrum. This gives rise to ill-conditioned equations. The values of the moments must, thus, be calculated to very high accuracy if the higher moments are to provide any extra information about these properties. Consequently, if more than twelve even moments are required, the evaluation has to be carried out using multilength working in the computer, whose single length register can hold up to eight significant digits.

The moments in this fcc lattice were first calculated on a Ferranti Mercury computer to double length accuracy, i.e., 16 significant figures. The program was later converted to triple length,[20] i.e., 24 significant figures. The first 34 even moments are given in Table I together with the displaced moments defined by

$$V_{2n}=\int_0^1(1-x^2)^n g(x)dx\,, \tag{29}$$

so that on expanding $(1-x^2)^n$,

$$V_{2n}=\sum_0^n\binom{n}{r}(-1)^r u_{2r}\,. \tag{30}$$

The spectrum can be derived by the use of an orthogonal polynomial expansion. If $P_n(x)$ is an orthogonal set of polynomials in the range $|x|\leqslant 1$, the spectrum can be expanded as

$$g(x)=\sum_0^\infty P_n(x)a_n\,, \tag{31}$$

where

$$a_n=\int_{-1}^{+1}P_n(x)g(x)dx\,. \tag{32}$$

The coefficients can be evaluated directly in terms of the moments. The spectrum using 21 and 22 even moments in a Legendre polynomial expansion is shown in Fig. 1, together with the spectrum obtained mechanically by Leighton.[18] Unfortunately full use could not be made of the 34 moments as triple length working is not available on the University of London Computer, where this work was carried out. The convergence of this expansion is slow. This is due to the singularities which occur in the spectrum, and are characteristic of a three-dimensional lattice. By locating the position of these singularities,[13] the behavior of the spectrum at these

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[19] H. W. Turnbull, *Theory of Equations* (Oliver & Boyd, London, 1939).

[20] I am grateful to C. E. Phelps of the Oxford Computing Laboratory for performing this transformation.

TABLE I. The moments of the fcc lattice; U_{2n} is the $2n$th normalized moment and V_{2n} is the $2n$th normalized displaced moment. These are both given in floating point convention i.e. $a, b=a\times10^b$.

n	U_{2n}	V_{2n}
0	1.00000 00000 00000 00000 000, 0	1.00000 00000 00000 00000 000, 0
1	5.00000 00000 00000 00000 000, −1	5.00000 00000 00000 00000 000, −1
2	3.12500 00000 00000 00000 000, −1	3.12500 00000 00000 00000 000, −1
3	2.22656 25000 00000 00000 000, −1	2.14843 75000 00000 00000 000, −1
4	1.71630 85937 50000 00000 000, −1	1.56005 85937 50000 00000 000, −1
5	1.38824 46289 06250 00000 000, −1	1.17767 33398 43750 00000 000, −1
6	1.15787 50610 35156 25000 000, −1	9.16786 19384 76562 50000 000, −2
7	9.85897 77946 47216 79687 500, −2	7.32203 72200 01220 70311 909, −2
8	8.51962 08208 79936 21826 185, −2	5.97683 89910 45951 84325 169, −2
9	7.44508 52349 40052 03247 072, −2	4.97144 85183 35819 24436 864, −2
10	6.56434 12235 65861 58275 604, −2	4.20330 06611 74580 45481 356, −2
11	5.83080 37721 87209 68812 699, −2	3.60485 57874 89213 98074 056, −2
12	5.21226 44747 32819 50806 261, −2	3.13042 33418 38195 48348 026, −2
13	4.68549 89484 37327 72642 388, −2	2.74836 14603 83819 12166 366, −2
14	4.23319 55658 39764 64025 896, −2	2.43629 83450 20304 62357 692, −2
15	3.84210 72315 61048 27502 574, −2	2.17811 93812 61861 55423 775, −2
16	3.50188 35779 01526 97199 255, −2	1.96201 96309 48347 56589 344, −2
17	3.20430 09673 17510 88735 813, −2	1.77921 69632 61716 74901 154, −2
18	2.94273 57727 35107 58415 298, −2	1.62308 47888 63482 28318 557, −2
19	2.71179 25621 81928 99416 762, −2	1.48855 70595 39037 05606 652, −2
20	2.50703 45201 16797 13098 531, −2	1.37171 33673 23317 43133 433, −2
21	2.32478 35129 10221 62065 313, −2	1.26948 52816 42612 00516 437, −2
22	2.16196 89284 78080 48542 815, −2	1.17944 56190 06111 53617 295, −2
23	2.01601 15088 44515 15502 348, −2	1.09965 52847 50039 13191 066, −2
24	1.88473 28210 08826 03275 203, −2	1.02855 06292 85414 69291 120, −2
25	1.76628 38580 92625 57463 887, −2	9.64859 67740 22976 91897 972, −3
26	1.65908 81429 45816 53901 046, −2	9.07539 17759 14862 47747 225, −3
27	1.56179 59788 27420 10708 711, −2	8.55726 83035 36202 58334 456, −3
28	1.47324 73720 76300 35907 933, −2	8.08704 69759 60147 36731 355, −3
29	1.39244 17729 43705 75964 459, −2	7.65870 92860 91062 75317 634, −3
30	1.31851 32271 55876 94419 981, −2	7.26717 72905 05374 21518 013, −3
31	1.25070 98567 71010 12099 665, −2	6.90814 05736 08361 93131 894, −3
32	1.18837 68304 68219 44941 274, −2	6.57791 93073 54590 48222 326, −3
33	1.13094 21647 89859 06965 998, −2	6.27335 50896 88701 99759 322, −3
34	1.07790 48356 71123 62285 800, −2	5.99172 33230 90801 98564 605, −3

points can be obtained. The effect of these singularities could then be subtracted out,[14] leaving a series whose convergence would be much improved.

It would not be difficult to get more moments on a faster multilength computer, if greater accuracy was required.

THE SPECIFIC HEAT AND OTHER THERMODYNAMIC FUNCTIONS

The specific heat and all the thermodynamic functions have high-temperature expansions in terms of the moments. The specific heat expansion is given by

$$\frac{C_v}{3N^3k}=\sum_{0}^{\infty}\frac{(2n-1)}{2n!}B_n u_{2n}\left(\frac{\Theta}{T}\right)^{2n}(-1)^{n+1}, \tag{33}$$

(B_n are the Bernoulli numbers) where $\Theta=h\nu_{\max}/k$. This series, however, diverges at $\Theta/T=2\pi$, i.e., $T/\Theta=0.159155$.

Domb and Isenberg[12] have shown that with 14 moments this series can be analytically continued, by the use of the Padé approximant, down to $(T/\Theta)\sim0.05$. Below this temperature the low-frequency expansion of the spectrum gives the accurate behavior of the specific heat. Two terms in the low-frequency expansion of the fcc lattice have already been obtained by Barron and Domb[21] so that the third term can be obtained approximately by extrapolating the displaced moments as discussed by Domb *et al.*[16] The low-frequency expansion, thus, gives

$$\nu_{\max}g(x)=2.6033x^2+4.639x^4+7.45x^6+\cdots. \tag{34}$$

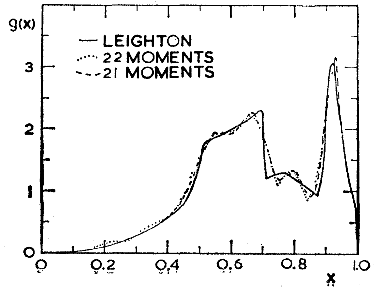

FIG. 1. Successive approximations to the spectrum of the fcc lattice using 21 and 22 even moments in a Legendre polynomial expansion, compared with that obtained by Leighton.

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[21] T. H. K. Barron and C. Domb, Proc. Roy. Soc. (London) A227, 447 (1955).

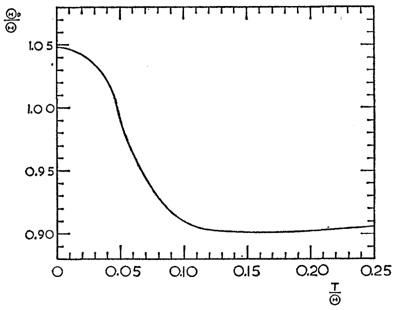

FIG. 2. The reduced equivalent Debye temperature Θ_D/Θ against T/Θ using a [15,18] Padé approximant to $(C_v/3N^3k)^2$ down to $(T/\Theta)=0.038$, and three terms in the low-temperature expansion for $(T/\Theta)<0.038$.

The last, extrapolated, coefficient is correct to 5%. At low temperatures the specific heat[22] becomes

$$\frac{C_v}{3N^3k}=2.6033\pi B_2\left(\frac{2\pi T}{\Theta}\right)^3+4.639\pi B_3\left(\frac{2\pi T}{\Theta}\right)^5+7.45\pi B_4\left(\frac{2\pi T}{\Theta}\right)^7+\cdots, \quad (35)$$

$$=0.27262\left(\frac{2\pi T}{\Theta}\right)^3+0.3470\left(\frac{2\pi T}{\Theta}\right)^5+0.78\left(\frac{2\pi T}{\Theta}\right)^7+\cdots. \quad (36)$$

The specific heat expressed in terms of the equivalent Debye temperature Θ_D is shown in Fig. 2 using 33 even moments in a [15,18] Padé approximant to C_v^2 which gives the correct low temperature T^3 behavior, down to $T/\Theta=0.0438$. Below this temperature (36) is used. Table II gives the coefficients in the Padé approximants, where A is the [15,18] Padé approximant to C_v^2, the coefficients a_r and b_r are given by

$$\left(\frac{C_v}{3N^3k}\right)^2[M,N]=\left[\sum_{r=0}^{M} a_r\left(\frac{\Theta}{T}\right)^{2r}\Big/\sum_{r=0}^{N} b_r\left(\frac{\Theta}{T}\right)^{2r}\right], \quad (37)$$

where $(C_v/3N^3k)^2[M,N]$ is the $[M,N]$ Padé approximant to $(C_v/3N^3k)^2$, B is the [16,18] Padé approximant to $(C_v/3N^3k)$ and is tabulated because C_v is more easily evaluated.

Figure 3 shows the fractional error $(\Delta C_v/C_v)$, plotted on a logarithmic scale, in the specific heat one may expect by using 33 even moments in a [15,18] Padé approximant for C_v^2, for a 1-dimensional model, and three terms in the low-temperature expansion. This was worked out for the monatomic linear chain with nearest neighbor interactions, for which C_v can be calculated exactly at all temperatures. The error is largest at $T/\Theta=0.038$ where its value is 1.4×10^{-4}. The fractional error rapidly decreases to less than 10^{-4} outside the range $0.056>T/\Theta>0.02$, becoming less than 10^{-6} outside the range $0.07>T/\Theta>0.012$. One may expect from the results of different Padé approximants and the low-temperature expansions, that the fractional error in the specific heat for this fcc model would be of the same order of magnitude as that for the linear chain.

The use of the Padé approximant together with the low-temperature expansion has enabled the specific heat to be outlined to an accuracy which at the very least is a factor of 10 better than any previous method, and over most of the temperature range is a factor of 10^2 better for $0.07<T/\Theta<0.012$.

THE ZERO-POINT ENERGY

Domb *et al.*[16] have shown that the zero-point energy of the lattice can most easily be obtained by expanding it in terms of the displaced moments, and correcting for the remaining unknown moments by means of the low-frequency expansion, to give

$$\frac{E_0}{N^3h\nu_{\max}}=\frac{3}{2}\left[\sum_{0}^{p-1} V_{2r}(-1)^r\binom{\frac{1}{2}}{r}-\frac{C_2}{16(2p+1)(2p-1)}-\frac{C_4}{2(2p+3)(2p+1)(2p-1)}-\frac{15C_6}{8(2p+5)(2p+3)(2p+1)(2p-1)}+\cdots\right], \quad (38)$$

where $p=35$, one greater than the number of moments calculated, and C_2, C_4, C_6 are the coefficients in the low frequency expansion of the spectrum as given in (34). Substituting into (38) from (34),

$$\frac{E_0}{N^3h\nu_{\max}}=1.022\,662\,15. \quad (39)$$

(Error of ±5 in the last decimal place.) The accuracy to

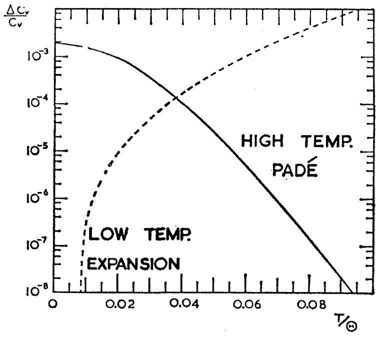

FIG. 3. A logarithmic plot of the accuracy of the specific heat $(\Delta C_v/C_v)$against (T/Θ) for the linear chain. The continuous curve is the accuracy of [16,17] Padé approximant to $(C_v/3N^3k)$ and the dashed curve the accuracy of three terms in the low-temperature expansion.

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[22] J. DeLaunay, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2.

TABLE II. A is the [15,18] Padé approximant to $(C_v/3N^3k)^2$ and B is the [16,18] Padé approximant to $(C_v/3N^3k)$. a_r and b_r are, respectively, the coefficients in the numerator and denominator of the Padé approximants. (Note: The coefficients are given in floating point convention where $a, b = a\times 10^b$.)

	A		B	
r	a_r	b_r	a_r	b_r
0	1.0000000, 0	1.0000000, 0	1.0000000, 0	1.0000000, 0
1	6.2510638, −2	1.4584397, −1	2.9295405, −2	7.0962071, −2
2	4.7317557, −4	8.2865620, −3	−2.4936205, −3	−8.3895082, −4
3	−4.2763040, −5	1.9691712, −4	−8.5237744, −5	−1.7577770, −4
4	−6.7556233, −7	−4.1804517, −7	1.2594683, −6	−3.3529944, −5
5	1.4988435, −8	−1.1884444, −7	4.3192132, −8	5.7077285, −8
6	2.8224286, −10	−1.6732481, −9	−8.1039094, −10	1.4736870, −9
7	−6.1735016, −12	2.0750606, −11	−1.3907575, −11	−2.8165452, −11
8	−2.2407414, −13	3.6248470, −13	3.9867657, −13	−4.9851083, −13
9	−2.8918513, −15	−2.3768265, −14	4.1511495, −15	1.4198298, −14
10	−2.0832640, −17	−9.9632230, −16	−1.4475964, −16	1.8914953, −16
11	−9.1582611, −20	−1.9104360, −17	−3.0210906, −18	−6.9669695, −18
12	−2.6585246, −22	−2.3019023, −19	−2.2573017, −20	−2.0758395, −19
13	−6.4914120, −25	−1.8982890, −21	−8.1667127, −23	−2.4399176, −21
14	−8.6855623, −28	−1.0982714, −23	−1.6777684, −25	−1.5625398, −23
15	−7.6880694, −31	−4.4215026, −26	−3.3282587, −28	−5.7248442, −26
16		−1.1896391, −28	2.8027457, −32	−1.1273250, −28
17		−1.9314971, −31		−9.1280289, −32
18		−1.4000082, −34		2.3615252, −35

which the zero point energy can be obtained illustrates well the power of the series expansion method.

CONCLUSIONS

The evaluation of large numbers of moments has enabled the thermodynamic properties to be obtained accurately, down to temperatures of $T/\Theta\sim 0.038$. The spectrum, on the other hand, can be obtained to high accuracy if one is prepared to locate the position of the critical points and the behavior of the spectrum near these points. Alternatively, if analytical methods fail to locate the singularities, the direct moment expansion can indicate their approximate position, and give an approximate spectrum.

Together, the moment expansion at high temperatures and the low-temperature expansion provide a more detailed knowledge of the equilibrium properties of crystals than has been previously obtained. The extension of the method to more complex unit cells, and larger range interactions is limited only by the time taken for the computation. At present, using the fastest computers, interactions between the first 30 nearest-neighbor atoms could be taken into account for crystals with cubic symmetry.

Results have also been obtained for other models of the fcc lattice, with second neighbor interactions, together with models of bcc, sc, and sq lattices. The only monatomic lattices with more than one atom per unit cell, for which moments have been calculated, is the hexagonal close packed. This lattice has a similar topology to that of the fcc which results in the two lattices having very similar moments. It is hoped to publish all these results in the future.

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