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# Note

## On the Low-Temperature Expansion of the Thermodynamical Integral for fcc Lattice

The thermodynamical integral

$$T_i(\alpha) = \frac{1}{(2\pi)^3} \iiint_{-\pi}^{\pi} \frac{dx\, dz\, dy}{\exp\{\alpha[1 - \gamma_i(x, y, z)]\} - 1} = \sum_{j=1}^{\infty} Q_i(j\alpha), \tag{1}$$

where

$$Q_i(j\alpha) = \frac{1}{\pi^3} \iiint_{0}^{\pi} \exp\{-\alpha j[1 - \gamma_i(x, y, z)]\}\, dx\, dy\, dz \tag{2}$$

and

$$\begin{aligned} \gamma_1(x, y, z) &= \tfrac{1}{3}(\cos x + \cos y + \cos z), \\ \gamma_2(x, y, z) &= \cos x \cos y \cos z, \\ \gamma_3(x, y, z) &= \tfrac{1}{3}(\cos x \cos y + \cos x \cos z + \cos y \cos z), \end{aligned} \tag{3}$$

for sc, bcc, and fcc lattices, respectively, has recently been evaluated for all cubic lattices [1]. However, the low-temperature (or large $\alpha$) expansion of $Q_i(j\alpha)$ used to obtain the low-temperature expansion of $T_i(\alpha)$ does not agree with that given by Joyce [2] for the bcc lattice and differs from that given below for the fcc lattice. This discrepancy is probably due to the fact that the asymptotic expansions have been used outside the region of their validity in the derivation of the final formula [1, Eqs. (35), (38)] by the former authors.[1]

In this paper we shall express the thermodynamical integral in terms of Mathieu functions and calculate the low-temperature expansion of $T_3(\alpha)$ using the method given by Sips [3].

In order to find the large $\alpha$ expansion of $T_3(\alpha)$ we shall first express $Q_3(j\alpha)$ in terms of Mathieu functions. Let us introduce the homogeneous integral equation [2, 5]

$$\frac{1}{\pi} \int_0^{\pi} \exp(\beta \cos x_i \cos x_j)\, \psi(x_j)\, dx_j = \lambda \psi(x_i), \tag{4}$$

[1] As pointed out by one of referees, this discrepancy is due to the misprints in [1]. Results of corrected formulas agree with that of Joyce [2] and that obtained in the present paper. However, [1 Eqs. (35)] (as well as corrected ones) give evidently wrong results in some cases, for example, $Q_2(\alpha, \eta, 1, 0, 0)$ is equal to 0 and $Q_2(\alpha, \eta, 1, 0, 0) \sim \alpha^{-3/2} \exp[-\alpha(\eta - 1)]$ for $\alpha$ large.

where $\beta = j\alpha/3$. The eigenfunctions of Eq. (4) are periodic even Mathieu functions

$$\begin{aligned} \psi_{2n}(x) &= ce_{2n}(x, -\beta^2/4), \\ \psi_{2n+1}(x) &= ce_{2n+1}(x, -\beta^2/4) \end{aligned} \tag{5}$$

defined by the Fourier series

$$\begin{aligned} ce_{2n}(x, q) &= \sum_{r=0}^{\infty} A_{2r}^{(2n)}(q) \cos 2rx, \\ ce_{2n+1}(x, q) &= \sum_{r=0}^{\infty} A_{2r+1}^{(2n+1)}(q) \cos(2r + 1)\, x. \end{aligned} \tag{6}$$

The eigenvalues $\lambda_n(\beta)$ are

$$\begin{aligned} \lambda_{2n}(\beta) &= A_0^{(2n)}(\beta^2/4)/ce_{2n}(0, \beta^2/4), \\ \lambda_{2n+1}(\beta) &= \beta/2\; B_1^{(2n+1)}(\beta^2/4)/se'_{2n+1}(0, \beta^2/4), \end{aligned} \tag{7}$$

where the periodic Mathieu function $se_{2n+1}$ is given by the Fourier series

$$se_{2n+1}(x, q) = \sum_{r=0}^{\infty} B_{2r+1}^{(2n+1)}(q) \sin(2r + 1)\, x. \tag{8}$$

The functions $\psi_n$ satisfy the orthogonality relation

$$\frac{2}{\pi} \int_0^{\pi} \psi_n(x)\, \psi_m(x)\, dx = \delta_{m,n}\,. \tag{9}$$

From Eqs. (4) and (9) and Mercer's expansion theorem it follows that

$$Q_3(\beta) = e^{-3\beta} \sum_{n=0}^{\infty} \lambda_n(\beta)^3. \tag{10}$$

It should be mentioned that Eq. (10) can be also obtained from the expression for the partition function of the Heisenberg model given in [6].

Sips [4] has shown that $\lambda_{2n}$ and $\lambda_{2n+1}$ have the same asymptotic expansion, so for large $\alpha$,

$$Q_3(\beta) = e^{-3\beta}\, 2 \sum_{n=0}^{\infty} \lambda_{2n}(\beta)^3 \tag{11}$$

($\lambda_{2n}$ introduced here is equal to $(2\pi\bar{\lambda}_{2n})^{-1}$ where $\bar{\lambda}_{2n}$ is the eigenvalue defined in [4]). The asymptotic expansion of $\lambda_{2n}$ can be evaluated from the equation [4]

$$\lambda_{2n}(\beta) = e^{\beta}[2\pi(2\beta)^{1/2}\, y_{2n}(K;0)]^{-1} \int_{-\infty}^{\infty} e^{-x^2/4}\Sigma(x)\, y_{2n}(K;x)\, dx, \tag{12}$$

where

$$\begin{aligned}\Sigma(x) &= (1 - x^2/2\beta)^{-1/2} \exp\{\beta[(1 - x^2/2\beta)^{1/2} - 1] + x^2/4\} \\ &= 1 + (1/2^5\beta)(2^3 \cdot x^2 - x^4) + (1/2^{11}\beta^2)(2^6 \cdot 3x^4 - 2^5 \cdot x^6 + x^8) \\ &\quad + (1/2^{16} \cdot 3 \cdot \beta^3)(2^9 \cdot 3 \cdot 5 \cdot x^6 - 2^5 \cdot 3^2 \cdot 5 \cdot x^8 + 2^3 \cdot 3^2 \cdot x^{10} - x^{12}) \\ &\quad + (1/2^{23} \cdot 3 \cdot \beta^4)(2^{12} \cdot 3 \cdot 5 \cdot 7 \cdot x^8 - 2^{12} \cdot 3 \cdot 7 \cdot x^{10} + 2^8 \cdot 3 \cdot 7 \cdot x^{12} \\ &\quad - 2^7 \cdot x^{14} + x^{16}) + \cdots\end{aligned} \tag{13}$$

and

$$y_{2n}(K;x) = \sum_{k=0}^{K} (2\beta)^{-k} \sum_{j=-2}^{2k} C_{k,2n+2j} D_{2n+2j}(x). \tag{14}$$

$D_n(x)$ are the parabolic cylinder functions and $C_{k,2n+2j}$ are the coefficients given for the first few $k$ in [3]. The recurrence relation for the coefficients $C_{k,2n+2j}$ can also be found here. $y_{2n}(K;x)$ must satisfy the differential equation [3]

$$[1 - (x^2/2\beta)]\, y_{2n}''(K;x) - (x/2\beta)\, y'(K;x) + [A - (x^2/4)]\, y_{2n}(K;x) = 0(\beta^{-k-1}), \tag{15}$$

with

$$A = 2n + \tfrac{1}{2} + (a_1/2\beta) + (a_2/(2\beta)^2) + \cdots. \tag{16}$$

It follows from Eqs. (14)–(16) that

$$a_{k+1} = \sum_{j=-2}^{2} \omega_{2n-2j,j} C_{k,2n-2j}\,, \tag{17}$$

$$\begin{aligned}C_{k+1,2n+2m} &= -\frac{1}{2m}\left\{\sum_{j=-2}^{2} \omega_{2n+2m-2j,j} C_{k,2n+2m-2j}\right. \\ &\qquad \left. - \sum_{j=1}^{k} a_j C_{k+1-j,2n+2m}\right\} \qquad \text{for} \quad m \neq 0, \\ &= 0 \qquad \text{for} \quad m = 0.\end{aligned} \tag{18}$$

$C_{0,2n} = 1$, the coefficients $\omega_{p,j}$ are of the form

$$\begin{aligned} &\omega_{p,2} = 1/4; \quad \omega_{p,1} = 1/2; \quad \omega_{p,0} = -(2p^2 + 2p + 1)/4; \\ &\omega_{p,-1} = -p(p-1)/2; \quad \omega_{p,-2} = p(p-1)(p-2)(p-3)/4; \end{aligned} \tag{19}$$

and it is assumed that $C_{i,2n+2j}$ vanish if either $2n + 2j < 0$ or $|j| > 2i$.

It has been shown in [4] that $\lambda_{2n}$ behaves asymptotically as $e^{\beta}\beta^{-n-(1/2)}$, so in the evaluation of $Q_3(\beta)$, for example, up to $\beta^{-15/2}$ only the first two terms of (11) need to be considered. The values of the first few coefficients $b_i$ in the expansion

$$Q_3(\beta) = \frac{1}{4(\pi\beta)^{3/2}} \sum_{i=0} b_i \beta^{-i} \tag{20}$$

are:

$$b_0 = 1; \quad b_1 = 3/8; \quad b_2 = 15/64; \quad b_3 = 107/512; \quad b_4 = 999/4096. \tag{21}$$

The combination of Eqs. (1) and (20) gives the required asymptotic expansion

$$T_3(\alpha) = \frac{1}{4(\pi\alpha/3)^{3/2}} \sum_{i=0} b_i \zeta(i + 3/2)(\alpha/3)^{-i}, \tag{22}$$

where $\zeta(m)$ is the Riemann zeta function[2]

$$\zeta(m) = \sum_{q=1}^{\infty} q^{-m}. \tag{23}$$

Equations (12)–(14) and (17)–(18), although not very easy to use, allow us to calculate an arbitrary number of terms in the asymptotic expansion of $Q_3(\beta)$ or $T_3(\alpha)$. Equation (10) can be used for the numerical evaluation of $Q_3(\beta)$ for an arbitrary $\beta > 0$. It should be mentioned that the first three coefficients of the expansion (22) agree with that given by Dyson [7] and obtained by him using physical rather than mathematical arguments.

## References

1. D. J. Austen and P. D. Loly, *J. Computational Phys.* **11** (1973), 315.
2. G. S. Joyce, *J. Math. Phys.* **12** (1971), 1390.
3. R. Sips, *Trans. Amer. Math. Soc.* **66** (1949), 93.
4. R. Sips, *Trans. Amer. Math. Soc.* **90** (1959), 340.

[2] For calculating the Reimann zeta function, see [8].

5. N. W. McLachlan, "Theory and Application of Mathieu Functions," Clarendon Press, Oxford, 1947.
6. G. S. Joyce, *Phys. Rev. Letters* **19** (1967), 581.
7. F. J. Dyson, *Phys. Rev.* **102** (1956), 1230.
8. W. J. Cody, K. E. Hillstrom, H. C. Thacher, Jr., *Math. Comp.* **25** (1971), 537.

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