Bicknese, V.
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THE THERMAL EXPANSION OF A FACE-CENTERED CUBIC LATTICE WITH CENTRAL TWO-BODY INTERACTIONS

by V. BICKNESE

Instituut voor theoretische fysica der Rijksuniversiteit te Utrecht, Nederland.

Synopsis

The thermal expansion ε is calculated by minimizing the free energy, including the cubic and quartic phonon-interaction terms. The free energy is expanded to third order in ε. The work is closely related to that of Maradudin[1]) and Maradudin, Flinn and Coldwell-Horsfall[2]). The resulting formulas are applied to the case of solid argon, for which the central interaction assumed may be considered rather realistic.

I. *Introduction.* To calculate observable properties of solid matter from the known (or supposedly known) interactions between constituting atoms is a challenging problem. In the case of thermal expansion the relevant theoretical formalism has recently been developed, but the actual calculation presents a formidable computational work. It requires among other things the evaluation of the vibration frequencies and polarisation vectors for many values of the lattice constant*).

It is the aim of the present paper to investigate in how far by making some approximations reasonably accurate values of the thermal expansion can be obtained without doing extensive numerical work. The method applied follows closely the work of Maradudin *e.a.*, but we shall try to improve upon their work in some respects.

The method of Maradudin[1]) consists in finding the phonon-frequencies ω as a function of the lattice constant by a first order perturbation treatment. The free energy, including the anharmonic terms, was calculated by Maradudin, Flinn and Coldwell-Horsfall[2]) for the case of a face-centered cubic lattice with central nearest-neigbour interactions in the limits of high and extremely low temperatures. By minimizing this free energy with respect to the lattice constant, one finds the thermal expansion at a given temperature.

*) We understand that such computations are presently being performed by F. W. de Wette and B. R. A. Nijboer, cf. Bull. Am. Phys. Soc. **10** (1965) 392.

The thermal expansion is defined as

$$\varepsilon(T) = \frac{r(T) - \tilde{r}}{\tilde{r}}$$

where $r(T)$ is the mean distance between two nearest neighbours at temperature T and $\tilde{r}$ is this distance in the static crystal.

In this paper all quantities which refer to the equilibrium distance calculated by minimizing the static energy are marked with a tilde ($\sim$).

II. *Expansion of the free energy to third order in* ε. We start from the following expression for the free energy[2]), which is exact to order $(u/d)^2$, where u is the average displacement and d is the lattice constant:

$$F = \frac{N}{2} \sum_l{}' \varphi(r_1) + \frac{1}{\beta} \sum_{\boldsymbol{k}j} \ln 2 \sinh \tfrac{1}{2}\beta\hbar\omega(\boldsymbol{k}j) - \frac{\hbar^2}{48N} \cdot$$

$$\cdot \sum_{\substack{\boldsymbol{k}_1\boldsymbol{k}_2\boldsymbol{k}_3 \\ j_1j_2j_3}} \frac{\Delta(\boldsymbol{k}_1 + \boldsymbol{k}_2 + \boldsymbol{k}_3)\, |\Phi(k_1j_1;\, k_2j_2;\, k_3j_3)|^2}{\omega(\boldsymbol{k}_1j_1)\, \omega(\boldsymbol{k}_2j_2)\, \omega(\boldsymbol{k}_3j_3)} \times$$

$$\times \prod_{s=1}^{3} \frac{1}{1 - \mathrm{e}^{-\beta\hbar\omega(\boldsymbol{k}_sj_s)}} \left[\frac{1 - \mathrm{e}^{-\beta\hbar(\omega(\boldsymbol{k}_1j_1) + \omega(\boldsymbol{k}_2j_2) + \omega(\boldsymbol{k}_3j_3))}}{\omega(\boldsymbol{k}_1j_1) + \omega(\boldsymbol{k}_2j_2) + \omega(\boldsymbol{k}_3j_3)} + \right.$$

$$\left. + 3 \frac{\mathrm{e}^{-\beta\hbar\omega(\boldsymbol{k}_3j_3)} - \mathrm{e}^{-\beta\hbar(\omega(\boldsymbol{k}_1j_1) + \omega(\boldsymbol{k}_2j_2))}}{\omega(\boldsymbol{k}_1j_1) + \omega(\boldsymbol{k}_2j_2) - \omega(\boldsymbol{k}_3j_3)} \right] +$$

$$+ \frac{\hbar^2}{32N} \sum_{\boldsymbol{k}_1\boldsymbol{k}_2j_1j_2} \frac{\Phi(\boldsymbol{k}_1j_1;\, \boldsymbol{k}_2j_2;\, -\boldsymbol{k}_1j_1;\, -\boldsymbol{k}_2j_2)}{\omega(\boldsymbol{k}_1j_1)\, \omega(\boldsymbol{k}_2j_2)} \frac{1 + \mathrm{e}^{-\beta\hbar\omega(\boldsymbol{k}_1j_1)}}{1 - \mathrm{e}^{-\beta\hbar\omega(\boldsymbol{k}_1j_1)}} \frac{1 + \mathrm{e}^{-\beta\hbar\omega(\boldsymbol{k}_2j_2)}}{1 - \mathrm{e}^{-\beta\hbar\omega(\boldsymbol{k}_2j_2)}} +$$

$$+ \ldots = F_1 + F_2 + F_3 + F_4 + \ldots \tag{II.1}$$

F_3 and F_4 are called respectively the cubic and the quartic anharmonic contributions to the free energy. N is the number of molecules in the crystal; $\varphi(r)$ is a two body potential. $\omega(\boldsymbol{k}j, r(T))$ are the $3N$ eigenfrequencies of the crystal with orthonormal polarization vectors $\boldsymbol{e}(\boldsymbol{k}j)$. $\Delta(\boldsymbol{k}) = 1$ if $\boldsymbol{k}$ is a vector of the reciprocal lattice and zero otherwise.

$$\Phi(\boldsymbol{k}_1j_1;\, \ldots \boldsymbol{k}_nj_n) = \frac{1}{2M^{n/2}} \sum_l \sum_{\alpha\beta\ldots\gamma} e_\alpha(\boldsymbol{k}_1j_1) \ldots e_\gamma(\boldsymbol{k}_nj_n)$$

$$\varphi_{\alpha\beta\ldots\gamma}(r_l) \prod_s (1 - \mathrm{e}^{-2\pi i \boldsymbol{k}_s r_l})$$

M is the mass of a molecule

$$\varphi_{\alpha\beta\ldots\gamma}(r_l) = \left(\frac{\partial^n}{\partial x_\alpha \ldots \partial x_\gamma} \varphi(r) \right)_{r=r_l}.$$

In particular:

$$\varphi_{\alpha\beta}(1) = \frac{x_\alpha x_\beta}{r^2}\left[\varphi''(r) - \frac{\varphi'(r)}{r}\right] + \frac{\delta_{\alpha\beta}}{r}\,\varphi'(r)/_{r=r_1}$$

$$\varphi_{\alpha\beta\gamma}(1) = \frac{x_\alpha x_\beta x_\gamma}{r^3}\left[\varphi'''(r) - \tfrac{3}{2}\varphi''(r) + \frac{3}{r^2}\,\varphi'(r)\right] +$$

$$+\left(\delta_{\alpha\beta}\frac{x_\gamma}{r^2} + \delta_{\beta\gamma}\frac{x_\alpha}{r^2} + \delta_{\gamma\alpha}\frac{x_\beta}{r^2}\right)\left[\varphi''(r) - \frac{\varphi'(r)}{r}\right]/_{r=r_1}$$

$$\varphi_{\alpha\beta\gamma\delta}(l) = \frac{x_\alpha x_\beta x_\gamma x_\delta}{r^4}\left[\varphi'^{\nu}(r) + \frac{6}{r}\,\varphi'''(r) + \frac{15}{r^2}\,\varphi''(r) - \frac{15}{r^3}\,\varphi'(r)\right] +$$

$$+\left(x_\alpha x_\beta\delta_{\gamma\delta} + x_\gamma x_\beta\delta_{\alpha\delta} + x_\gamma x_\alpha\delta_{\beta\delta} + x_\alpha x_\delta\delta_{\gamma\beta} + x_\beta x_\delta\delta_{\alpha\gamma} + x_\gamma x_\delta\delta_{\alpha\beta}\right)\frac{1}{r^3}$$

$$\left[\varphi'''(r) - \frac{3}{r}\,\varphi''(r) + \frac{3}{r^2}\,\varphi'(r)\right] +$$

$$+\left(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\beta\gamma}\delta_{\delta\alpha} + \delta_{\alpha\gamma}\delta_{\beta\delta}\right)\frac{1}{r^2}\left[\varphi''(r) - \frac{\varphi'(r)}{r}\right]/_{r=r_1}$$

We recall the following well known relation (cf. III):

$$\omega_{kj}^2 = \frac{2}{M}\sum_l{}'\left(\varphi'' - \frac{\varphi'}{r_l}\right)\left(\frac{\boldsymbol{r}_l\cdot\boldsymbol{e}_{kj}}{r_l}\right)^2 \sin^2\pi\boldsymbol{k}\cdot\boldsymbol{r}_l + \frac{2}{M}\sum_l{}'\frac{\varphi'}{r_l}\sin^2\pi\boldsymbol{k}\cdot\boldsymbol{r}_l \quad \text{(II 2)}$$

from which it follows, that

$$\sum_j \omega_{kj}^2 = \frac{2}{M}\sum_l{}'\left(\varphi'' + \frac{2\varphi'}{r_l}\right)\sin^2\pi\boldsymbol{k}\cdot\boldsymbol{r}_l. \quad \text{(II.3)}$$

Later on we shall make the approximation

$$\frac{2}{M}\left(\tilde{\varphi}'' + \frac{2\tilde{\varphi}'}{\tilde{r}}\right)\sum_{\text{n.n.}}\left(\frac{\boldsymbol{r}\cdot\boldsymbol{e}(\boldsymbol{k}_j)}{\tilde{r}}\right)^2 \sin^2\pi\boldsymbol{k}\cdot\boldsymbol{r} = \tilde{\omega}^2(\boldsymbol{k}_j). \quad \text{(II.4)}$$

(n.n. stands for nearest neighbours).

Let us now consider the terms of F separately for the case of a f.c.c. lattice:

1) $$F_1(\varepsilon) = \frac{N}{2}\sum_l{}'\,\varphi(\tilde{\boldsymbol{r}}_l(1+\varepsilon)) = \frac{N}{2}\sum_l{}'\,\varphi(\tilde{\boldsymbol{r}}_l) +$$

$$+\frac{N}{2}\frac{\varepsilon^2}{2}\sum_l{}'\,\tilde{\boldsymbol{r}}_l^2\varphi''(\tilde{\boldsymbol{r}}_l) + \ldots = P_1 + \varepsilon Q_1 + \tfrac{1}{2}\varepsilon^2 R_1 + \tfrac{1}{6}\varepsilon^3 S_1 + 0(\varepsilon^4) \quad \text{(II.5)}$$

where $Q_1 = 0$.

For a potential of the form

$$\varphi(r) = \frac{A}{r^m} - \frac{B}{r^n}$$

the lattice sums occurring here are known; they have been tabulated by Jones and Ingham[3]).

$$2)\quad F_2(\varepsilon) = \frac{1}{\beta} \sum_{kj} \ln 2 \sinh \tfrac{1}{2}\beta\hbar(\tilde{\omega}(kj) + \varepsilon A(kj) + \tfrac{1}{2}\varepsilon^2 B(kj) + \\ + \tfrac{1}{6}\varepsilon^3 C(kj) + 0(\varepsilon^4)).$$

We shall calculate A, B and C in the next section. We may write:

$$F_2(\varepsilon) = F_2(0) + \varepsilon \left[\frac{1}{\beta} \sum_{kj} \tfrac{1}{2}\beta\hbar A \coth \tfrac{1}{2}\beta\hbar\tilde{\omega}\right] + 0(\varepsilon^2) = \\ = P_2 + \varepsilon Q_2 + \tfrac{1}{2}\varepsilon^2 R_2 + \tfrac{1}{6}\varepsilon^3 S_2 + 0(\varepsilon^4). \qquad \text{(II.6)}$$

3) F_3 and F_4 which represent the contributions of the anharmonic terms are expected to be small compared to F_1. They may therefore be treated in an approximate way.

In F_4 we shall restrict ourselves to the contributions of the nearest neighbours.

$$F_4 = \frac{\hbar^2}{4NM^2} \sum_{\text{n.n.}} \left(\varphi'^{\text{v}} - 6\frac{\varphi'''}{r} + 15\frac{\varphi''}{r^3} - 15\frac{\varphi'}{r^3}\right) \cdot \\ \cdot \left\{\sum_{kj} \left(\frac{\boldsymbol{e}\cdot\boldsymbol{r}}{r}\right)^2 \frac{1}{\omega} \coth \tfrac{1}{2}\beta\hbar\omega \cdot \sin^2 \pi\boldsymbol{k}\cdot\boldsymbol{r}\right\}^2 + \\ + \frac{\hbar^2}{4NM^2} \sum_{\text{n.n.}} \left(\frac{\varphi'''}{r} - \frac{3\varphi''}{r^2} + \frac{3\varphi'}{r^3}\right) \left[4 \sum_{\gamma} \left\{\sum_{\alpha} \sum_{kj} \frac{x_\alpha e_\alpha e_\gamma}{r\omega} \coth \tfrac{1}{2}\beta\hbar\omega \sin^2 \pi\boldsymbol{k}\cdot\boldsymbol{r}\right\}^2 + \right. \\ \left. + 2\left\{\sum_{kj} \left(\frac{\boldsymbol{e}\cdot\boldsymbol{r}}{r}\right)^2 \frac{\sin^2 \pi\boldsymbol{k}\cdot\boldsymbol{r}}{\omega} \coth \tfrac{1}{2}\beta\hbar\omega\right\} \left\{\sum_{kj} \frac{1}{\omega} \coth \tfrac{1}{2}\beta\hbar\omega \sin^2 \pi\boldsymbol{k}\cdot\boldsymbol{r}\right\}\right] + \\ + \frac{\hbar^2}{4NM^2} \sum_{\text{n.n.}} \left(\frac{\varphi''}{r^2} - \frac{\varphi'}{r^3}\right) \left[2 \sum_{\alpha\gamma} \left\{\sum_{kj} \frac{e_\alpha e_\gamma}{\omega} \coth \tfrac{1}{2}\beta\hbar\omega \sin^2 \pi\boldsymbol{k}\cdot\boldsymbol{r}\right\}^2 + \right. \\ \left. + \left\{\sum_{kj} \frac{1}{\omega} \coth \tfrac{1}{2}\beta\hbar\omega \sin^2 \pi\boldsymbol{k}\cdot\boldsymbol{r}\right\}^2\right].$$

Here one may raise the question in how far it is consistent to neglect the contributions from neighbours beyond the nearest on the one hand and on the other hand to keep in the above expression terms like

$$\frac{\varphi'''}{r}, \quad \frac{\varphi''}{r^2} \text{ and } \frac{\varphi'}{r^3}$$

in addition to φ'^{v}. One may notice that e.g. $\varphi''' \sim 10\,\varphi''/r$.

Maradudin e.a. accordingly use the so-called Leibfried approximation

and neglect these terms, i.e. they take

$$F_4 = \frac{\hbar^2}{4NM^2} \sum_{\text{n.n.}} \varphi'^{\text{v}} \left\{ \sum_{kj} \left(\frac{\boldsymbol{e}\cdot\boldsymbol{r}}{r} \right)^2 \frac{1}{\omega} \coth \tfrac{1}{2}\beta\hbar\omega \sin^2 \pi \boldsymbol{k}\cdot\boldsymbol{r} \right\}^2. \quad \text{(II.7)}$$

As we shall see, however, this approximation can change the value of the quartic contributions quite substantially. Therefore we shall not use it. One can also make a partial Leibfried approximation by keeping in addition to φ'^{v} only φ'''/r. The above expression is still too complicated to handle without extensive numerical work. Therefore we now use the approximation (II.4). This approximation consists of three parts:

1) We assume that only nearest neighbour interactions are important.
2) We choose the potential dependent part of the expression in such a way, that $\sum_j \tilde{\omega}_j^2$ has the correct value.
3) We consider $\boldsymbol{e}$ independent of the lattice constant. As we shall see in section III this is correct in the case of only nearest neighbour interactions.

With this approximation we can simplify the expression for F_4 in the partial Leibfried approximation mentioned above (see ref. 2 p. 365 for an analogous calculation):

$$F_4 = \frac{\varphi'^{\text{v}} - 6\dfrac{\varphi'''}{r}}{48N\left(\tilde{\varphi}'' + 2\dfrac{\tilde{\varphi}'}{\tilde{r}}\right)^2} \left(\sum_{kj} \tfrac{1}{2}\hbar \frac{\tilde{\omega}^2}{\omega} \coth \tfrac{1}{2}\beta\hbar\omega \right)^2 + \frac{4\dfrac{\varphi'''}{r}}{48N\left(\tilde{\varphi}'' + 2\dfrac{\tilde{\varphi}'}{\tilde{r}}\right)^2} \cdot$$

$$\cdot \left\{ \left(\sum_{kj} \tfrac{1}{2}\hbar \frac{\tilde{\omega}^2}{\omega} \coth \tfrac{1}{2}\beta\hbar\omega \right)^2 + \right.$$

$$\left. + \tfrac{1}{2} \left(\sum_{kj} \tfrac{1}{2}\hbar \frac{\tilde{\omega}^2}{\omega} \coth \tfrac{1}{2}\beta\hbar\omega \right) \left(\sum_{kj} \tfrac{1}{2}\hbar \frac{\sum_{j'} \tilde{\omega}^2(\boldsymbol{k}j')}{\omega} \coth \tfrac{1}{2}\beta\hbar\omega \right) \right\} \quad \text{(II.8)}$$

Finally we write

$$\sum_{kj} \tfrac{1}{2}\hbar \frac{\sum_{j'} \tilde{\omega}^2(\boldsymbol{k}j')}{\omega(\boldsymbol{k}j)} \coth \tfrac{1}{2}\beta\hbar\omega(\boldsymbol{k}j) = \alpha(T) \sum_{kj} \tfrac{1}{2}\hbar \frac{\tilde{\omega}^2(\boldsymbol{k}j)}{\omega(\boldsymbol{k}j)} \coth \tfrac{1}{2}\beta\hbar\omega(\boldsymbol{k}j) \quad \text{(II.9)}$$

$\alpha(T)$ could be calculated numerically as a function of temperature as soon as we knew $\tilde{\omega}(\boldsymbol{k}j)$ for many points in the Brillouin zone. Without embarking upon such an extensive program, we shall be content in the following estimates to use 2 values of α independent of temperature, viz. $\alpha = 3$ (obtained when $\tilde{\omega}$ does not depend on polarization) and $\alpha = 4$. We then have:

$$F_4 = \frac{\varphi'^{\text{v}} + (2\alpha - 2)\dfrac{\varphi'''}{r}}{48N\left(\tilde{\varphi}'' + 2\dfrac{\tilde{\varphi}'}{\tilde{r}}\right)^2 N} \left(\sum_{kj} \tfrac{1}{2}\hbar \frac{\tilde{\omega}^2}{\omega} \coth \tfrac{1}{2}\beta\hbar\omega \right)^2. \quad \text{(II.10)}$$

If we do not wish to use Leibfried approximation at all, we can proceed by assuming that one of the following substitutions is allowed:

$$\sum_{kj} \frac{e_x^2}{\omega} \coth \tfrac{1}{2}\beta\hbar\omega \sin^2 \frac{\pi r}{\sqrt{2}} (k_x + k_y) = \sum_{kj} \frac{e_z^2}{\omega} \coth \tfrac{1}{2}\beta\hbar\omega \sin^2 \frac{\pi r}{\sqrt{2}} (k_x + k_y) \tag{II.11}$$

or alternatively

$$\sum_{kj} \frac{\mathrm{e}_x \mathrm{e}_y}{\omega} \coth \tfrac{1}{2}\beta\hbar\omega \sin^2 \frac{\pi r}{\sqrt{2}} (k_x + k_y) = 0.$$

For $\alpha = 3$ these two assumptions are aequivalent and we find:

$$F_4 = \frac{\left(\varphi'^{\mathrm{v}} + 4\dfrac{\varphi'''}{r}\right)}{48N\left(\tilde{\varphi} + \dfrac{2\tilde{\varphi}'}{\tilde{r}}\right)^2} \left(\sum_{kj} \tfrac{1}{2}\hbar \frac{\tilde{\omega}^2}{\omega} \coth \tfrac{1}{2}\beta\hbar\omega\right)^2. \tag{II.12}$$

This is exactly the same result as with the partial Leibfried approximation. For $\alpha = 4$ we find:

$$F_4 = \frac{\left(\varphi'^{\mathrm{v}} + 6\dfrac{\varphi'''}{r} + \dfrac{55}{9}\dfrac{\varphi''}{r^2} - \dfrac{55}{9}\dfrac{\varphi'}{r^3}\right)}{48N\left(\tilde{\varphi}'' + 2\dfrac{\tilde{\varphi}'}{\tilde{r}}\right)^2} \left(\sum_{kj} \tfrac{1}{2}\hbar \frac{\tilde{\omega}^2}{\omega} \coth \tfrac{1}{2}\beta\hbar\omega\right)^2$$

on using the first and

$$F_4 = \frac{\left(\varphi'^{\mathrm{v}} + 6\dfrac{\varphi'''}{r} + 7\dfrac{\varphi''}{r^2} - 7\dfrac{\varphi'}{r^3}\right)}{48N\left(\tilde{\varphi}'' + 2\dfrac{\varphi'}{\tilde{r}}\right)^2} \left(\sum_{kj} \tfrac{1}{2}\hbar \frac{\tilde{\omega}^2}{\omega} \coth \tfrac{1}{2}\beta\hbar\omega\right)^2$$

on using the second assumption. These expressions deviate only slightly from the one obtained in the partial Leibfried approximation. In the following for $\alpha = 4$ we shall adopt an intermediate expression:

$$F_4 = \frac{\left(\varphi'^{\mathrm{v}} + 6\dfrac{\varphi'''}{r} + \dfrac{13}{2}\dfrac{\varphi''}{r^2} - \dfrac{13}{2}\dfrac{\varphi'}{\mathrm{r}^3}\right)}{48N\left(\tilde{\varphi}'' + 2\dfrac{\tilde{\varphi}'}{\tilde{r}}\right)^2} \left(\sum_{kj} \tfrac{1}{2}\hbar \frac{\tilde{\omega}^2}{\omega} \coth \tfrac{1}{2}\beta\hbar\omega\right)^2. \tag{II.13}$$

We can now expand F_4 with respect to ε. For $\alpha = 4$ we find:

$$F_4(\varepsilon) = F_4(0) + \frac{\varepsilon}{48N\left(\tilde{\varphi}'' + 2\frac{\tilde{\varphi}'}{\tilde{r}}\right)^2}\left[\left(\tilde{r}\tilde{\varphi}^{\text{v}} + 6\tilde{\varphi}'^{\text{v}} + \tfrac{1}{2}\frac{\tilde{\varphi}'''}{\tilde{r}} - \right.\right.$$

$$\left. - \frac{39}{2}\frac{\tilde{\varphi}''}{\tilde{r}^2} + \frac{39}{2}\frac{\tilde{\varphi}'}{\tilde{r}^3}\right)\left(\sum_{kj} \tfrac{1}{2}\hbar\tilde{\omega}\coth\tfrac{1}{2}\beta\hbar\tilde{\omega}\right)^2 +$$

$$+ \left(2\tilde{\varphi}'^{\text{v}} + 12\frac{\tilde{\varphi}'''}{\tilde{r}} + 13\frac{\tilde{\varphi}''}{\tilde{r}^2} - 13\frac{\tilde{\varphi}'}{\tilde{r}^3}\right)\left(\sum_{kj} \tfrac{1}{2}\hbar\tilde{\omega}^2\coth\tfrac{1}{2}\beta\hbar\tilde{\omega}\right)\cdot$$

$$\left.\cdot\left(-\sum_{kj}\tfrac{1}{2}\hbar A\coth\tfrac{1}{2}\beta\hbar\tilde{\omega} - \sum_{kj}\frac{\tfrac{1}{4}\beta\hbar^2 A\tilde{\omega}}{\sinh^2\tfrac{1}{2}\beta\hbar\tilde{\omega}}\right)\right] + 0^{(\epsilon^2)} =$$

$$= P_4 + \varepsilon Q_4 + \tfrac{1}{2}\varepsilon^2 R_4 + \tfrac{1}{6}\varepsilon^3 S_4 + 0(\varepsilon^4) \tag{II.14}$$

where $A(\boldsymbol{kj})$ is the same function as in (II.6).

It may be remarked here, that the substitution (II.9) can be made after the expansion has been performed. Then we are only concerned with quantities which refer to the harmonic approximation. The result will be the same.

4) For F_3 it is not so easy to give a similar treatment. We therefore just take over the results of reference 2 calculated numerically in the Leibfried approximation and in the limits of high and extremely low temperatures, while only nearest neighbour-interaction was taken into account.

High energy limit:

$$F_3 = \frac{-172{,}3}{3072} N(kT)^2 \frac{(\varphi''')^2}{(\varphi'')^3}$$

and expanded in ε:

$$F_3(\varepsilon) = F_3(0) + \varepsilon\tilde{r}\left(\frac{2\tilde{\varphi}'^{\text{v}}}{\tilde{\varphi}'''} - \frac{3\tilde{\varphi}'''}{\tilde{\varphi}''}\right)F_3(0) + 0(\varepsilon^2)$$

$$= P_3 + \varepsilon Q_3 + \tfrac{1}{2}\varepsilon^2 h_3 + \tfrac{1}{6}\varepsilon^3 S_3 + 0(\varepsilon^4). \tag{II.15}$$

Low temperature limit:

$$F_3 = -\frac{1}{96}\frac{\hbar^2}{M}\left(\frac{\varphi'''}{\varphi''}\right)^2 N(1{,}481) - 0{,}0808\frac{M}{\hbar^2}\frac{(\varphi''')^2}{(\varphi'')^4}(kT)^4 N\cdot$$

$$\cdot F_3(\varepsilon) = F_3(0) + \varepsilon\tilde{r}\left\{\left(\frac{2\tilde{\varphi}'^{\text{v}}}{\tilde{\varphi}'''} - \frac{2\tilde{\varphi}'''}{\tilde{\varphi}''}\right)\frac{-1}{96}\frac{\hbar^2}{M}\frac{(\tilde{\varphi}''')^2}{(\tilde{\varphi}'')^2}N(1{,}481) - \right.$$

$$\left. - \left(\frac{2\tilde{\varphi}'^{\text{v}}}{\tilde{\varphi}'''} - \frac{4\tilde{\varphi}'''}{\tilde{\varphi}''}\right)0{,}0808\frac{M}{\hbar^2}\frac{(\tilde{\varphi}''')^2}{(\tilde{\varphi}'')^4}(kT)^4 N\right\} + 0(\varepsilon^2). \tag{II.16}$$

III. *Calculation of* $A(\boldsymbol{k}j)$, $B(\boldsymbol{k}j)$ and $C(\boldsymbol{k}j)$. $\omega(\boldsymbol{k}j)$ is determined by the eigenvalue problem

$$\sum_{\beta} D_{\alpha\beta}(\boldsymbol{k})\, e_{\beta}(\boldsymbol{k}j) = \omega^2(\boldsymbol{k}j)\, e_{\alpha}(\boldsymbol{k}j) \tag{III.1}$$

with

$$D_{\alpha\beta}(\boldsymbol{k}) = \frac{2}{M} \sum_{l}{}' \left(\left(\varphi'' - \frac{\varphi'}{r} \right) \frac{x_\alpha x_\beta}{r^2} + \frac{\varphi'}{r}\, \delta\alpha\beta \right) \sin^2 \pi \boldsymbol{k}\cdot\boldsymbol{r}. \tag{III.2}$$

From the orthonormality of the polarization vectors it follows that:

$$\omega^2(\boldsymbol{k}j) = \frac{2}{M} \sum_{l}{}' \left(\varphi'' - \frac{\varphi'}{r} \right) \left(\frac{\boldsymbol{r}\cdot\boldsymbol{e}}{r} \right)^2 \sin^2 \pi \boldsymbol{k}\cdot\boldsymbol{r} + \frac{2}{M} \sum_{l}{}' \frac{\varphi'}{r} \sin^2 \pi \boldsymbol{k}\cdot\boldsymbol{r} \tag{II.2}$$

and multiplying by e_α:

$$\frac{2}{M} \sum_{l}{}' \left(\varphi'' - \frac{\varphi'}{r} \right) \frac{x_\alpha}{r} \left(\frac{\boldsymbol{r}\cdot\boldsymbol{e}}{r} \right) \sin^2 \pi \boldsymbol{k}\cdot\boldsymbol{r} = \frac{2}{M} \sum_{l}{}' e_\alpha \left(\varphi'' - \frac{\varphi'}{r} \right) \cdot \left(\frac{\boldsymbol{r}\cdot\boldsymbol{e}}{r} \right)^2 \sin^2 \pi \boldsymbol{k}\cdot\boldsymbol{r}. \tag{III.3}$$

In the case of nearest-neighbour interaction only, this reduces to:

$$\sum_{\text{n.n.}} x_\alpha (\boldsymbol{r}\cdot\boldsymbol{e}) \sin^2 \pi \boldsymbol{k}\cdot\boldsymbol{r} = \sum_{\text{n.n.}} (\boldsymbol{r}\cdot\boldsymbol{e})^2\, e_\alpha \sin^2 \pi \boldsymbol{k}\cdot\boldsymbol{r}. \tag{III.4}$$

e is then determined by the structure of the crystal only and does not depend on the distance between nearest neighbours. We now assume also for the general case, that $\boldsymbol{e}$ is independent of $\boldsymbol{r}$. This assumption can be shown to be equivalent with the first order perturbation treatment used in ref. 1. We then find from (II.2)

$$\omega^2 - \tilde{\omega}^2 = \frac{2}{M} \left\{ \sum_{l}{}' \left(\frac{\boldsymbol{r}\cdot\boldsymbol{e}}{r} \right)^2 \sin^2 \pi \boldsymbol{k}\cdot\boldsymbol{r} \cdot \right.$$
$$\cdot \left(\varepsilon \tilde{r} \tilde{\varphi}''' + \tfrac{1}{2}\varepsilon^2 \tilde{r}^2 \tilde{\varphi}'^{\nu} + \ldots - \frac{\dfrac{\tilde{\varphi}'}{\tilde{r}} + \varepsilon\tilde{\varphi}'' + \tfrac{1}{2}\varepsilon^2 \tilde{r} \tilde{\varphi}'''}{1+\varepsilon} + \frac{\tilde{\varphi}'}{\tilde{r}} \right) +$$
$$+ \sum_{l}{}' \sin^2 \pi \boldsymbol{k}\cdot\boldsymbol{r} \left(\frac{\dfrac{\tilde{\varphi}'}{\tilde{r}} + \varepsilon\tilde{\varphi}'' + \tfrac{1}{2}\varepsilon^2 \tilde{r} \tilde{\varphi}''' \ldots}{1+\varepsilon} - \frac{\tilde{\varphi}'}{\tilde{r}} \right). \tag{III.5}$$

This can be written as follows:

$$\omega^2 - \tilde{\omega}^2 = \varepsilon\Big[-8\tilde{\omega}^2 + \frac{2}{M}\sum_l{}'\Big(\tilde{\varphi}'''\tilde{r} + 7\tilde{\varphi}'' - 7\frac{\tilde{\varphi}'}{\tilde{r}}\Big)\cdot$$

$$\cdot\Big(\frac{\boldsymbol{r}\cdot\boldsymbol{e}}{r}\Big)^2 \sin^2 \pi\boldsymbol{k}\cdot\boldsymbol{r} + \frac{2}{M}\sum_l{}'\Big(\tilde{\varphi}'' + 7\frac{\tilde{\varphi}'}{\tilde{r}}\Big)\sin^2 \pi\boldsymbol{k}\cdot\boldsymbol{r}\Big] +$$

$$+ \tfrac{1}{2}\varepsilon^2\Big[72\tilde{\omega}^2 + \frac{2}{M}\sum_l{}'\Big(\tilde{r}^2\tilde{\varphi}'^{\mathrm{v}} - \tilde{r}\tilde{\varphi}''' - 70\tilde{\varphi}'' + 70\frac{\tilde{\varphi}'}{\tilde{r}}\Big)\cdot$$

$$\cdot\Big(\frac{\boldsymbol{r}\cdot\boldsymbol{e}}{r}\Big)^2 \sin^2 \pi\boldsymbol{k}\cdot\boldsymbol{r} + \frac{2}{M}\sum_l{}'\Big(\tilde{r}\tilde{\varphi}''' - 2\tilde{\varphi}'' - 70\frac{\tilde{\varphi}'}{\tilde{r}}\Big)\sin^2 \pi\boldsymbol{k}\cdot\boldsymbol{r}\Big] +$$

$$+ \tfrac{1}{6}\varepsilon^3\Big[-720\tilde{\omega}^2 + \frac{2}{M}\sum_l{}'\Big(\tilde{r}^3\tilde{\varphi}^{\mathrm{v}} - \tilde{r}^2\tilde{\varphi}'^{\mathrm{v}} + 3\tilde{r}\tilde{\varphi}''' + 714\tilde{\varphi}'' - 714\frac{\tilde{\varphi}'}{\tilde{r}}\Big)\cdot$$

$$\cdot\Big(\frac{\boldsymbol{r}\cdot\boldsymbol{e}}{r}\Big)^2 \sin^2 \pi\boldsymbol{k}\cdot\boldsymbol{r} + \frac{2}{M}\sum_l{}'\cdot$$

$$\cdot\Big(\tilde{r}^2\tilde{\varphi}'^{\mathrm{v}} - 3\tilde{r}\tilde{\varphi}''' + 6\tilde{\varphi}'' + 714\frac{\tilde{\varphi}'}{\tilde{r}}\Big)\sin^2 \pi\boldsymbol{k}\boldsymbol{r}\Big] + 0(\varepsilon^4). \qquad \text{(III.6)}$$

If we assume, that at greater distances the potential is of the form $\varphi = -B/r^6$, all coefficients under the summation signs turn out to cancel. We may then restrict ourselves to a small number of neighbours. Here it must be kept in mind, that for higher derivatives the repulsive term grows more important, e.g. if

$$\varphi = \frac{A}{r^{12}} - \frac{B}{r^6}$$

we find for the next-nearest-neighbour value of $r^4\varphi'^{\mathrm{v}}$: $(512 - 756)\, A/r_1^{12}$ if we take as subsidiary condition, that $\varphi'(r_1) = 0$.

We shall keep here only the nearest neighbours, i.e. for a (12,6) Lennard-Jones potential the repulsion forces are neglected beyond the nearest neighbours.

A, B and C could now be calculated quite easily by numerical computation if we knew $\tilde{\omega}(\boldsymbol{k}j)$ and $\boldsymbol{e}(\boldsymbol{k}j)$. In this paper we wish to avoid extensive numerical calculations as far as possible and accordingly make the following approximations.

$$\sum_{\text{n.n.}} \sin^2 \pi\boldsymbol{k}\cdot\boldsymbol{r} = \frac{\frac{M}{2}\sum_j \tilde{\omega}^2 - \sum_{\text{non n.n.}}\Big(\tilde{\varphi}'' + \frac{2\tilde{\varphi}'}{\tilde{r}}\Big)\sin^2 \pi\boldsymbol{k}\cdot\boldsymbol{r}}{\tilde{\varphi}'' + 2\frac{\tilde{\varphi}'}{\tilde{r}}} \approx \frac{\frac{M}{2}\alpha\tilde{\omega}^2}{\tilde{\varphi}'' + 2\frac{\tilde{\varphi}'}{\tilde{r}}}$$

(α is defined in (II.9)) and

$$\sum_{\text{n.n.}} \left(\frac{\boldsymbol{r}\cdot\boldsymbol{e}}{r}\right)^2 \sin^2 \pi\boldsymbol{k}\cdot\boldsymbol{r} =$$

$$= \frac{\frac{M}{2}\tilde{\omega}^2 - \frac{\tilde{\varphi}'}{\tilde{r}}\left(\frac{\frac{M}{2}\sum_j \tilde{\omega}^2}{\tilde{\varphi}'' + 2\frac{\tilde{\varphi}'}{\tilde{r}}}\right) - \sum_{\text{n.n.n.}} \left(\tilde{\varphi}'' - \frac{\tilde{\varphi}'}{r}\right)\left(\frac{\boldsymbol{r}\cdot\boldsymbol{e}}{r}\right)^2 \sin^2\boldsymbol{k}\cdot\boldsymbol{r}}{\tilde{\varphi}'' - \frac{\tilde{\varphi}'}{\tilde{r}}} +$$

$$+ \frac{\frac{\tilde{\varphi}'}{\tilde{r}\tilde{\varphi} + 2\tilde{\varphi}'} \sum_{\text{n.n.n.}} \left(\tilde{\varphi}'' + 2\frac{\tilde{\varphi}'}{\tilde{r}}\right) \sin^2 \pi\boldsymbol{k}\cdot\boldsymbol{r}}{\tilde{\varphi}'' - \frac{\tilde{\varphi}'}{\tilde{r}}} \approx \frac{\frac{M}{2}\tilde{\omega}^2\left(\tilde{\varphi}'' + (2-\alpha)\frac{\tilde{\varphi}'}{\tilde{r}}\right)}{\left(\tilde{\varphi}'' + 2\frac{\varphi'}{\tilde{r}}\right)\left(\tilde{\varphi}'' - \frac{\varphi'}{\tilde{r}}\right)}. \tag{III.7}$$

We think to make a smaller error by applying this approximation to (III.6) than by making a restriction to nearest neighbours interactions straight in (III.5). With $\omega^2 - \tilde{\omega}^2 = (\omega - \tilde{\omega})(\omega + \tilde{\omega}) = (\varepsilon A + \frac{1}{2}\varepsilon^2 B + \frac{1}{6}\varepsilon^3 (+ \ldots)(2\tilde{\omega} + \varepsilon A + \frac{1}{2}\varepsilon^2 B + \ldots)$. we now find in a simple way for $\alpha = 4$:

$$A(\boldsymbol{k}j) = \tilde{\omega}\,\frac{-8\left(\tilde{\varphi}'' + \frac{2\tilde{\varphi}'}{\tilde{r}}\right)\left(\tilde{\varphi}'' - \frac{\tilde{\varphi}'}{\tilde{r}}\right) + \left(\tilde{\varphi}''\tilde{r} + 7\tilde{\varphi}'' - 7\frac{\tilde{\varphi}'}{\tilde{r}}\right)\left(\tilde{\varphi}'' - 2\frac{\tilde{\varphi}'}{\tilde{r}}\right) + 4\left(\tilde{\varphi}'' + 7\frac{\tilde{\varphi}'}{\tilde{r}}\right)\left(\tilde{\varphi}'' - \frac{\tilde{\varphi}'}{\tilde{r}}\right)}{2\left(\tilde{\varphi}'' + \frac{2\tilde{\varphi}'}{\tilde{r}}\right)\left(\tilde{\varphi}'' - \frac{\tilde{\varphi}'}{\tilde{r}}\right)} \tag{III.8}$$

Similar formulae can be computed for B and C. We omit them here for brevity.

We remark, that there is a small difference between

$$\left(\sum_{\boldsymbol{k}j} \frac{\sum_{j'} \omega^2(j')}{\omega} \coth \tfrac{1}{2}\beta\hbar\omega\right)^2 \text{ and } \left(\sum_{\boldsymbol{k}j} \frac{(\sum_{j'} \omega^2(j'))^2}{\omega^3} \coth \tfrac{1}{2}\beta\hbar\omega\right)(\sum_{\boldsymbol{k}j} \omega \coth \tfrac{1}{2}\beta\hbar\omega).$$

This can be indicated by $(\alpha)^2 \neq \alpha^2$. For instance for $\alpha = 4$ we shall take $\alpha^2 = 20$ and $\alpha^3 = 120$. As a consequence there is a small difference between

$$(\sum A \coth \tfrac{1}{2}\beta\hbar\omega)^2 \text{ and } \left(\sum \frac{A^2}{\omega} \coth \tfrac{1}{2}\beta\hbar\omega\right)(\sum \omega \coth \tfrac{1}{2}\beta\hbar\omega).$$

This is indicated by $(A(\boldsymbol{k}j))^2 \neq A^2(\boldsymbol{k}j)$.

When the expressions for A, B and C are substituted in the results of the preceding section, we see, that we have expressed all interesting quantities

in the derivatives of φ at the point $\tilde{r}$ and in

$$\sum_{kj} \tfrac{1}{2}\hbar\tilde{\omega} \coth \tfrac{1}{2}\beta\hbar\tilde{\omega} = \tilde{E}(T)$$

and its derivatives with respect to temperature.

IV. *Example and conclusions.* The effect of the various approximations made is of course dependent on the potential we choose. We shall take here as an example a Lennard-Jones potential

$$\varphi = \frac{A}{r^{12}} - \frac{B}{r^6}$$

with the coefficients used by Domb and Zucker[4]) for argon

$$(A = 1.6310^{-7}\ \text{Å}^{12}\text{erg},\ B = 1.0510^{-10}\ \text{Å}^6\ \text{erg}).$$

We do not expect to get close agreement with experiment with this potential, which has been criticized by several authors. It may serve here as an example. We use the cgs unit system.

We give some results as an illustration of the influence of the used approximations:

$NQ_2 = -8.46\tilde{E}(T)$ no Leibfried appr. $\alpha = 4$; $\alpha^2 = 20$; $\alpha^3 = 120$

$NQ_2 = -8.72\tilde{E}(T)$ no Leibfried appr. $\alpha = 3$; $\alpha^2 = 9$; $\alpha^3 = 27$

$NQ_2 = -9.72\tilde{E}(T)$ Leibfried approximation

$NR_2 = 66.7\tilde{E} + 71.8\beta \dfrac{d\tilde{E}}{d\beta}$ no Leibfried appr. $\alpha = 4$

$NR_2 = 69.0\tilde{E} + 76.0\beta \dfrac{d\tilde{E}}{d\beta}$ no Leibfried appr. $\alpha = 3$

$NR_2 = 71.4\tilde{E} + 85.9\beta \dfrac{dE}{d\beta}$ Leibfried approximation

$N^2Q_4 = 6 \times 10^{11}\tilde{E}^2 - 353 \times 10^{11}\tilde{E}\beta \dfrac{d\tilde{E}}{d\beta}$ no Leibfried $\alpha = 4$

$N^2Q_4 = -17 \times 10^{11}\tilde{E}^2 - 416 \times 10^{11}\tilde{E}\beta \dfrac{dE}{d\beta}$ no Leibfried $\alpha = 3$.

We do not give the quartic anharmonic terms in the Leibfried approximation, because it is clear that this approximation will not give very good results in this case, where the cases $\alpha = 3$ and $\alpha = 4$ show already a relatively big difference. We were, however, not able to circumvent this approximation when calculating F_3. Neither were we able to extend this calculation to intermediate temperatures. An extensive numerical computation would be

necessary here. As we shall see, however, the anharmonic terms are small, in particular at low temperatures. So it is good enough for the moment to use the expression for high temperatures also at somewhat lower temperatures.

Also for the precise determination of $\alpha(T)$ a numerical treatment would be necessary. We give in table I values for 0°K and for 80°K. It is assumed, that for 80°K we may apply the above formulae in the high temperature limit. Where possible we did not use the Leibfried approximation. We adopted $\alpha = 4$. The static term was evaluated to fourth order in ε.

$$\tilde{E}(80°) = 240kN = 3.31 \times 10^{14}N$$

$$\tilde{E}(0°) = 1.02N\hbar \frac{8\left(\tilde{\varphi}'' + \dfrac{2\tilde{\varphi}'}{r}\right)}{M} = 1.5 \times 10^{-14}N(5).$$

The Debye temperature for argon is 84°K.

The melting temperature is 83.8°K.

TABLE I

0°K			
$Q_1 = 0$	$R_1 = 12.0 \times 10^{-12}$	$S_1 = -245 \times 10^{-12}$	
$Q_2 = -12.8 \times 10^{-14}$	$R_2 = 1.01 \times 10^{-12}$	$S_2 = -13.4 \times 10^{-12}$	
$Q_3 = -2.09 \times 10^{-16}$	$R_3 = 4.46 \times 10^{-15}$	$S_3 = -3.8 \times 10^{-12}$	
$Q_4 = 1.38 \times 10^{-16}$	$R_4 = 1.4 \times 10^{-14}$	$S_4 = 0.5 \times 10^{-12}$	
$Q = -12.8 \times 10^{-14}$	$R = 13.0 \times 10^{-12}$	$S = -262 \times 10^{-12}$	
80°K			
$Q_1 = 0$	$R_1 = 12.0 \times 10^{-12}$	$S_1 = -245 \times 10^{-12}$	$T_1 = 43 \times 10^{-10}$
$Q_2 = -28.0 \times 10^{-14}$	$R_2 = 0.2 \times 10^{-12}$	$S_2 = -15.5 \times 10^{-12}$	
$Q_3 = -2.17 \times 10^{-14}$	$R_3 = -0.5 \times 10^{-12}$	$S_3 = -15.4 \times 10^{-12}$	
$Q_4 = 3.94 \times 10^{-14}$	$R_4 = 0.8 \times 10^{-12}$	$S_4 = 26.5 \times 10^{-12}$	
$Q = -26.3 \times 10^{-14}$	$R = 12.5 \times 10^{-12}$	$S = -249 \times 10^{-12}$	$T = 43 \times 10^{-10}$

At $T = 0$°K the anharmonic terms are seen to be practically negligible. ε can now be calculated from $Q + \varepsilon R + \frac{1}{2}\varepsilon^2 S = 0$, giving

$$\varepsilon = 0.011 \text{ for } T = 0°\text{K}$$

and

$$\varepsilon = 0.027 \text{ for } T = 80°\text{K}$$

Neglecting S gives an underestimation of ε with about 11% in the first case. When using a fourth order expansion we get:

$$Q + \varepsilon R + \tfrac{1}{2}\varepsilon^2 s + \tfrac{1}{6}\varepsilon^3 T = 0.$$

Neglecting S and T gives an error of about 25%, while neglect of T only gives an error of 7% for 80°K.

We notice, that even near the melting temperature the anharmonic terms

play a rather modest part. Here one must keep in mind, however, that near the melting point anharmonic terms beyond F_4 may grow more important. We notice, that e.g. $S_4 > -S_2$.

We compare the values of ε, calculated above, with those calculated from the rough formula

$$\varepsilon_M = -\frac{1}{12}\frac{\tilde{E}}{N}\frac{\tilde{\varphi}'''}{\tilde{r}(\tilde{\varphi}'')^2}$$

used by Maradudin in his articles. This formula deviates not very much from ours, when neglecting S. $\varepsilon_M(0°K) = 0.010$ $\varepsilon_M(80°K) = 0.022$. The experimental values for argon are $\varepsilon(0°K) = 0.017$ and $\varepsilon(80°K) = 0.045$)[6]. The disagreement with experiments is partly due to the approximations made in the evaluation of the expression for the free energy, which can only be avoided by making extensive numerical computations of frequencies and polarization vectors. But to a large extend this disagreement is probably due to the choice of the Lennard Jones potential for the interaction between argon atoms.

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