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THE INFLUENCE OF UNHARMONIC EFFECTS ON SPECIFIC HEAT

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Abstract: The specific heat at constant pressure is calculated on the basis of a model which includes the following assumptions: 1) the interaction exists only between the neighbour particles and depends only on their distance; 2) for small distances from the equilibrium position, the interaction is approximately harmonic; 3) the mean value of the particle position does not coincide with its equilibrium position; 4) the change of the particle arrangement is allowed. The specific heat is then given by the following expression:

$$C_p = Nk\left(\frac{1}{2} - a + a^2 \frac{d^2 \ln \Gamma(a)}{d a^2}\right), \qquad aT = 480.$$

The computed values are compared with the experimental results for tungsten. Near the melting point the measured values are greater than the computed ones. This indicates that some other effects exist which are not included in this simple model.

1. Introduction

Several important characteristics of the crystal lattice can be explained by the unharmonicity of forces acting between the lattice particles, as, for example, the thermal expansion, the change of specific heat with pressure and temperature, heat conductivity, etc. For this reason the investigation of the influence of unharmonicity within the classical temperature range is important for better understanding of properties of crystal lattice. Nevertheless, in the analysis of these problems in the case of three-dimensional lattice, considerable difficulties arise. Therefore, one-dimensional lattices are investigated for wich the working models could be more precisely defined with the effect that the mathematical treatment becomes, at least in principle, less difficult. It is obvious that the extension of these results to the three-dimensional lattice, should be undertaken with certain precaution, because of the inherent limitations of any one-dimensional model. But even in the case of an one-dimensional model, there are difficulties due to the fact that the analysis is mainly numerical and the mathematical treatment is rather tedious. There are certain models of one-dimensional lattice, where only the interaction between the neighbour particles of the lattice is considered[1, 2] which are illustrative enough mainly because the results are given in analytical form. This is also the purpose of the present paper.

2. *One-dimensional model*

One-dimensional lattice with $N+1$ particles of equal mass will be considered, in which the interaction exists only between the neighbour particles depending only on their relative distance. Additionally, forces of constant intensity $P > 0$ are supposed (this corresponds to the pressure in a three-dimensional case), acting in opposite directions on the last two particles. If $x = \{x_0, x_1, \dots, x_N\}$ represents the set of all coordinates of the particles relative to the coordinate system fixed at an arbitrary point on the line on which all the particles are lying, the total energy of the system is

$$H = \frac{1}{2} m \sum_{i=0}^{N} \dot{x}_i^2 + \sum_{i=0}^{N-1} V(x_{n+1} - x_n) - P(x_N - x_0) = \frac{1}{2} m \sum_{i=0}^{N} \dot{x}_i^2 +$$

$$+ \sum_{i=0}^{N-1} [V(x_{n+1} - x_n) - P(x_{n+1} - x_n)] .$$

Applying the transformation

$$A = \begin{pmatrix} \frac{1}{N+1} & \frac{1}{N+1} & \frac{1}{N+1} & \dots & \frac{1}{N+1} \\ -1 & 1 & 0 & \dots & 0 \\ 0 & -1 & 1 & \dots & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & \dots & 1 \end{pmatrix},$$

new coordinates $z = Ax$ can be introduced. From the transformation it follows that

$$z_0 = \frac{1}{N+1} \sum_{i=0}^{N} x_i$$

is the coordinate of the centre of mass, while $z_i = x_{i+1} - x_i$ $(i = 1, 2 \ldots, N)$ are the relative coordinates. Since det $A \neq 0$, the inverse transformation A^{-1} is possible, so that $x = A^{-1}z$. If the last equation is differentiated with respect to time and the result introduced into the expression for kinetic energy, then

$$T = \frac{1}{2} m \, (\dot{x}, \dot{x}) = \frac{1}{2} m \, (A'^{-1} A^{-1} \dot{z}, \dot{z}) = \frac{1}{2} m \, (B \dot{z}, \dot{z}) \, ,$$

where $B = A'^{-1} A^{-1}$ (A' is the transposed matrix). From the last equation new impulses may be found:

$$p_i = \frac{\partial T}{\partial z_i} = m \sum_{j=0}^{N} b_{ij} \dot{z}_j \, ,$$

where b_{ij} are the matrix elements of the symmetric matrix B. The last equation may be written in the following way:

$$p = m B \dot{z} \, ,$$

where $p = \{ p_0, p_1, \ldots, p_N \}$. The total energy may be expressed as

$$H = \frac{1}{2m} (p, AA'p) + \sum_{i=1}^{N} [V(z_i) - Pz_i] \, .$$

Since $AA' = \frac{1}{N+1} + C$, where

$$C = \left\{ \begin{array}{ccccc} 2 & -1 & 0 & \ldots & 0 \\ -1 & 2 & -1 & \ldots & 0 \\ 0 & -1 & 2 & \ldots & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & \ldots & 2 \end{array} \right\} ,$$

taking the origin of the CS to be in the centre of mass, the total energy may be expressed as

$$H = \frac{1}{2m} \sum_{i,\, j=1}^{N} c_{ij} p_i p_j + \sum_{i=1}^{N} [V(z_i) - Pz_i] \, ,$$

where c_{ij} are the matrix elements of the symmetric matrix C. The statistical integral of the system is

$$Z(\vartheta)=\int e^{-\frac{\vartheta}{2m}\sum_{i,j=1}^{N} c_{ij}\,p_i\,p_j}\,dp_1\ldots dp_N\int e^{-\vartheta\sum_{i=1}^{N}[(Vz_i)-Pz_i]}\,dz_1\ldots dz_N,$$

where $\vartheta = 1/kT$, and the integration is performed over the whole phase space. Since C represents the nonnegative symmetric matrix and det $C = N + 1$, it follows that the proper values λ_i are real positive numbers in which case $\prod_{i=1}^{N}\lambda_i = N + 1$. With regard that there exists an orthogonal transformation T which diagonalizes the matrix C, we may use new variables $P = Tp$. Then the integral over the impuls space becomes

$$\int e^{-\frac{\vartheta}{2m}\sum_{i=1}^{N}\lambda_i P_i^2}\,dP_1\ldots dP_N=\frac{1}{\sqrt{N+1}}\left(\frac{2\pi m}{\vartheta}\right)^{\frac{N}{2}},$$

and the statistical integral is

$$Z(\vartheta)=\frac{1}{\sqrt{N+1}}\left(\frac{2\pi m}{\vartheta}\right)^{\frac{N}{2}}\left[\int_{-\infty}^{+\infty} e^{-\vartheta[V(z)-Pz]}\,dz\right]^{N},$$

Suppose the potential function has the following form:

$$V(z) = V_0\,[e^{a(z-d)} - a\,(z-d) - 1]\,,$$

where a, V_0 and d are positive constants (d is the distance between the neighbour equilibrium positions). For $z = d$ this function has a minimum value. When developed in series around this point, the harmonic approximation is obtained from its first term. The function increases asymmetrically around the point $z = d$, indicating that the mean value of the particle position does not coincide with the equilibrium position. If the function $V(z)$ is introduced in the statistical integral, one obtains

$$Z(\vartheta)=\frac{1}{\sqrt{N+1}}\left(\frac{2\pi m\,V_0}{a^2}\right)^{\frac{N}{2}}\left[\frac{e^{\beta\left(1+\frac{Pd}{V_0}\right)}\,\Gamma(\alpha)}{\beta^{\alpha+1/2}}\right]^{N}, \qquad (1)$$

where $\beta = \vartheta V_0$ and $\alpha = \beta\left(1 + \frac{aV_0}{P}\right)$. From Eq. (1) it is posisble to calculate the specific heat at constant pressure

$$\frac{C_p}{Nk} = \frac{1}{2} - \alpha + \alpha^2 \frac{d^2 \ln \Gamma(\alpha)}{d\alpha^2} \equiv F(\alpha) , \qquad \alpha = \frac{V_0 (1 + \frac{P}{aV_0})}{kT} . \qquad (2)$$

Since

$$\alpha^2 \frac{d^2 \ln \Gamma(\alpha)}{d\alpha^2} = 1 + \alpha^2 \sum_{k=1}^{\infty} \frac{1}{(k + \alpha)^2} ,$$

it follows that $\lim_{\alpha \to 0} F(\alpha) = 3/2$, while from

$$\alpha^2 \frac{d^2 \ln \Gamma(\alpha)}{d\alpha^2} = \alpha + \frac{1}{2} + \sum_{m=1}^{K} (-1)^{m-1} \frac{Bm}{\alpha^{2m-1}} + O\left(\frac{1}{\alpha^{2K+1}}\right) ,$$

where B_m are Bernoulli numbers, it comes out $\lim_{\alpha \to +\infty} F(\alpha) = 1$. Between these values, the function $F(\alpha)$ decreases monotonously with increasing α, i. e. the specific heat increases monotonously with the temperature, Table 1.

Table 1

α	0	0,5	1	2	4	6	8	10	$+\infty$
C_p/Nk	1,500	1,234	1,145	1,080	1,041	1,028	1,020	1,015	1,000

If in Eq. (3) the terms including α^{-3} are retained, Eq. (2) has approximately the following form:

$$\frac{C_p}{Nk} = 1 + \frac{1}{6\alpha} - \frac{1}{30\alpha^3} \doteq 1 + \frac{1}{6}\frac{kT}{C} - \frac{1}{30}\left(\frac{kT}{C}\right)^3 , \qquad (4)$$

where $C = V_0 (1 + \frac{P}{\alpha V_0})$. As it can be seen, no term in Eq. (4) is proportional to the square of the temperature.

3. *Comparison with the experiment*

It should be noted that so far no approximations have been made. From Eq. (1) we can easily evaluate the free energy and calculate the main thermodynamic properties of the linear chain such as compressibility, thermal expansion, electrical resistivity, etc. Before starting any systematic study based on this model it is important to establish whether this model can account for any of the observed deviations from classical harmonic behavior. In order to compare the model with the experiment, we have chosen the specific heat at constant pressure of tungsten. The second row of the Table 2 gives the experimental values of the specific heat of tungsten⁽³⁾ (in calories per mol and per degree). The third row gives the results based on our model and the fourth row the results obtained on the basis of the Morse potential in the approximation for condensed state⁽¹⁾.

Table 2

T	400	600	800	1200	1600	2400	2600	3600
C_p (exp)	6,70	6,87	6,92	7,33	7,68	8,30	9,00	14,70
C_p (th)	6,70	6,98	7,20	7,53	7,76	8,05	—	—
C_p (Morse)	6,70	7,08	7,44	8,19	8,95	10,44	—	—

Since the experimental errors may amount up to 3%, the computed values are in very good agreement with the experimental ones in the temperature interval from 600 °K to 2400 °K. At 2600 °K the experimental value of the specific heat reaches already the maximum value obtained from Eq. (2). Further increase of the specific heat with temperature indicates that some other effects exist which in this simple model were not taken into account. Some of the recent measurements⁽³⁾ indicate that the formation of the lacunae, the concentration of which in the vicinity of the point of fusion of tungsten amounts up to 2,42%, is the main reason for this discrepancy.

It should be mentioned here that the experimental value of the specific heat at 400 °K was used for the determination of the only undetermined parameter in Eq. (2) (as well as in the calculation based on the Morse potential, where, in addition, the depth of the potential has been taken to be 203 Cal.⁽⁴⁾. In this way the relation between the parameter α and the temperature is found to be

$$\alpha T = 480.$$

The essential points of our model are its mathematical simplicity and its capability to reproduce some experimental results. These facts determined the choice of the potential function. In order to establish the full validity of the model it will be necessary to carry out the calculations of the thermodynamic properties other than the specific heat and for some elements other than tungsten. It is our feeling that the model could explain some other deviations from the classical harmonic behavior of the crystal lattice.

References

1) J. S. Dugdale, D. K. C. MacDonald, Phys. Rev. **96** (1954) 57;
2) D. K. C. MacDonald, S. K. Roy, Phys. Rev. **97** (1955) 673;
3) C. Affortit, CEA — R 3287 (1967);
4) J. C. Slater, Introduction to Chemical Physics, McGraw-Hill New York, (1963).

UTICAJ NEHARMONIJSKIH EFEKATA NA SPECIFIČNU TOPLOTU

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Sadržaj

U radu je izvršeno izračunavanje specifične toplote pri konstantnom pritisku uz pomoć modela zasnovanog na ovim pretpostavkama: 1) interakcija postoji samo između susednih čestica i zavisi samo o njihovom međusobnom rastojanju; 2) za mala rastojanja čestica od položaja ravnoteže, interakcija je približno harmonijska; 3) srednje vrednosti položaja čestica ne poklapaju se s njihovim položajima ravnoteže; 4) dozvoljena je izmena poretka čestica. Pored spomenutih osobina, interakcija mora biti tako odabrana, da se rezultati mogu dobiti u zatvorenom analitičkom obliku. Posmatrani model je jednodimenzion i njegovo upoređenje s eksperimentalnim rezultatima izvršeno je uz dodatnu pretpostavku, da se kretanje svake čestice u tri dimenzije može razložiti na tri međusobno nezavisne komponente, pri čemu se svaka komponenta kreće u potencijalnom polju definisanim tim modelom. Izračunavanje statističkog integrala u sistemu centra masa svodi se na integraciju po impulsnom delu prostora i na N integrala sa istim podintegralnim funkcijama od samo jedne promenljive — relativne koordinate. Prvi integral se ortogonalnom transformacijom, koja uvek postoji, može svesti na Poissonov integral dok se druga integracija može svesti na integral, koji je već poznat u matematičkoj literaturi.

Jedn. (1) daje rešenje statističkog integrala odakle se može izvesti jedn. (2) koja daje specifičnu toplotu pri konstantnom pritisku. Izračunate vrednosti upoređene su s merenjima specifične toplote volframa pri konstantnom pritisku3) i modelom, koji se zasniva na Morzeovom potencijalu1). Drugi red u Tablici 2 daje eksperimentalne rezultate, treći daje rezultate, koji se dobivaju na osnovu opisanog modela, dok poslednji red daje vrednosti izračunate po modelu, u čijoj osnovi stoji Morzeov potencijal. Kao što se iz tablice vidi, u intervalu između 600 °K i 2400 °K slaganje je dobro jer eksperimentalni rezultati dozvoljavaju grešku do 3%. U blizini tačke topljenja volframa merene vrednosti su iznad izračunatih, što se objašnjava stvaranjem lakuna, koji efekt nije obuhvaćen modelom.